

# INTERNATIONAL ATOMIC WEIGHTS.....

September, 1940 No.....

(Logarithms introduced by the Author).....

Name.	Sym- bol.	Atomic weight.	Loga- rithm.	Volume No.	Sym- bol.	Atomic weight.	Loga- rithm.
Aluminium	Al	26.97	1.4309	Molybdenum	Mo	95.93	1.9820
Antimony	Sb	121.76	2.0855	Neodymium	Nd	144.27	2.1592
Argon	A	39.944	1.6015	Neon	Ne	20.183	1.3050
Arsenic	As	74.91	1.8746	Nickel	Ni	58.69	1.7686
Barium	Ba	137.36	2.1379	Nitrogen	N	14.008	1.1464
Beryllium	Be	9.02	0.9552	Osmium	Os	190.2	2.2792
Bismuth	Bi	209.00	2.3201	Oxygen	O	16.0000	1.2041
Boron	B	10.82	1.0342	Palladium	Pd	106.7	2.0282
Bromine	Br	79.910	1.9026	Phosphorus	P	30.98	1.4911
Cadmium	Cd	112.41	2.0507	Platinum	Pt	195.23	2.2905
Cæsium	Cs	132.91	2.1236	Potassium	K	39.098	1.5921
Calcium	Ca	40.08	1.6030	Praseodymium	Pr	140.92	2.1489
Carbon	C	12.010	1.0795	Protoactinium	Pa	231	2.3636
Cerium	Ce	140.13	2.1465	Radium	Ra	226.05	2.3542
Chlorine	Cl	35.457	1.5490	Radon	Rn	222	2.3464
Chromium	Cr	52.01	1.7161	Rhenium	Re	186.31	2.2702
Cobalt	Co	58.94	1.7701	Rhodium	Rh	102.91	2.0123
Columbium	Cb	92.91	1.9680	Rubidium	Rb	85.48	1.9319
Copper	Cu	63.57	1.8033	Ruthenium	Ru	101.7	2.0072
Dysprosium	Dy	162.46	2.2106	Samarium	Sm	150.43	2.1773
Erbium	Er	167.2	2.2232	Scandium	Sc	45.10	1.6512
Europium	Eu	152.0	2.1818	Selenium	Se	78.96	1.8974
Fluorine	F	19.00	1.2788	Silicon	Si	28.06	1.4481
Gadolinium	Gd	156.9	2.1956	Silver	Ag	107.880	2.0329
Gallium	Ga	69.72	1.8433	Sodium	Na	22.997	1.3617
Germanium	Ge	72.60	1.8609	Strontium	Sr	87.63	1.9420
Gold	Au	197.2	2.2949	Sulphur	S	32.06	1.5059
Hafnium	Hf	178.6	2.2519	Tantalum	Ta	180.88	2.2574
Helium	He	4.003	0.6024	Tellurium	Te	127.61	2.1050
Holmium	Ho	164.94	2.2173	Terbium	Tb	159.2	2.2020
Hydrogen	H	1.0080	0.0033	Thallium	Tl	204.39	2.3104
Indium	In	114.70	2.0598	Thorium	Th	232.12	2.3657
Iodine	I	126.92	2.1035	Thulium	Tm	169.4	2.2290
Iridium	Ir	193.1	2.2853	Tin	Sn	118.70	2.0743
Iron	Fe	55.85	1.7470	Titanium	Ti	47.90	1.6803
Krypton	Kr	83.7	1.9227	Tungsten	W	183.92	2.2646
Lanthanum	La	138.92	2.1428	Uranium	U	238.07	2.3767
Lead	Pb	207.21	2.3164	Vanadium	V	50.93	1.7071
Lithium	Li	6.940	0.8414	Xenon	Xe	131.3	2.1183
Lutecium	Lu	174.99	2.2430	Ytterbium	Yb	173.04	2.2381
Magnesium	Mg	24.32	1.3860	Yttrium	Y	88.92	1.9490
Manganese	Mn	54.93	1.7398	Zinc	Zn	65.38	1.8154
Mercury	Hg	200.61	2.3023	Zirconium	Zr	91.22	1.9601

*Note.* This Table is given in full for the convenience of those who wish to consult a Table of Atomic Weights for any purpose. It is recognised that many of the elements will never be met with in the ordinary course of analysis, and that in many cases the atomic weights are given to a degree of accuracy which is seldom required.

# QUANTITATIVE CHEMICAL ANALYSIS .

**THE PLANT ALKALOIDS**

By THOMAS ANDERSON HENRY, D.Sc. *Third Edition.*  
45s.

**THE NATURAL ORGANIC TANNINS**

By M. NIERENSTEIN, D.Sc. 21s.

**THE CHEMICAL ANALYSIS OF FOODS**

By H. E. COX, Ph.D., D.Sc., F.I.C. *Second Edition.*  
41 Illustrations. 21s.

**RECENT ADVANCES IN PHYSICAL CHEMISTRY**

By S. GLASSTONE, Ph.D., D.Sc., F.I.C. *Third Edition.*  
31 Illustrations. 15s.

**THE THEORY OF EMULSIONS AND THEIR  
TECHNICAL TREATMENT**

By W. CLAYTON, D.Sc., F.I.C. *Fourth Edition*  
103 Illustrations. 42s.

**SUTTON'S SYSTEMATIC HANDBOOK OF  
VOLUMETRIC ANALYSIS**

*Twelfth Edition.* by A. D. MITCHELL, D.Sc., F.I.C.  
128 Illustrations. 35s.

**ALLIANCE COMMERCIAL ORGANIC ANALYSIS**

F  
C  
a

**ORGANIC**

revised by JULIUS GRANT,  
preparation.

**HACKH'S CHEMICAL DICTIONARY**

Contains over 57,000 words generally used in  
Chemistry and many of the Terms used in  
Related Sciences.

By JULIUS GRANT, M.Sc., Ph.D., F.R.I.C. *Third  
Edition* 232 Illustrations. Over 100 Tables. 50s.

**J. & A. CHURCHILL Ltd.**

CLOWES AND COLEMAN'S  
QUANTITATIVE  
CHEMICAL ANALYSIS

AN INTERMEDIATE TEXT-BOOK

EDITED AND REVISED BY  
**JULIUS GRANT**  
M.Sc., Ph.D.(Lond.), F.R.I.C.

FIFTEENTH EDITION

*Thirty-fifth Thousand*

With 143 Illustrations



LONDON  
**J. & A. CHURCHILL LTD.**  
104 GLOUCESTER PLACE  
PORTMAN SQUARE  
1944

.. BOMBAY, 127. THIS IS FROM  
NEW BOOK CO., BOMBAY



FIRST EDITION	.	.	.	<i>November 1891</i>
SECOND	"	.	.	<i>January 1894</i>
THIRD	"	.	.	<i>September 1895</i>
FOURTH	"	.	.	<i>August 1897</i>
FIFTH	"	.	.	<i>August 1900</i>
SIXTH	"	.	.	<i>March 1903</i>
SEVENTH	"	.	.	<i>October 1905</i>
"	"	(reprinted)	.	<i>February 1907</i>
"	"	"	.	<i>August 1908</i>
EIGHTH	"	.	.	<i>September 1909</i>
NINTH	"	.	.	<i>September 1911</i>
TENTH	"	.	.	<i>November 1913</i>
ELEVENTH	"	.	.	<i>January 1918</i>
"	"	(reprinted)	.	<i>January 1921</i>
TWELTH	"	.	.	<i>January 1924</i>
THIRTEENTH	"	.	.	<i>September 1931</i>
FOURTEENTH	"	.	.	<i>January 1938</i>
FIFTEENTH	"	.	.	<i>May 1944</i>

# PREFACE TO THE FIFTEENTH EDITION

IN preparing the new Edition the principal function of this book, as stated by the original authors, has been kept prominently in mind. However, although this function was essentially that of an intermediate textbook, paying special regard to the requirements of senior students, the writer could not ignore his own experience of it as a valuable stand-by when he has been called upon to carry out analyses outside his current everyday experience. Since, to his knowledge, the value in this respect of past editions has been fully recognised by analysts in general, it has been allowed to influence to some extent the nature of the present revisions and additions.

Apart from some rearrangements, such as the transfer of the section on Soap from Foodstuffs to Oils, Fats and Waxes, the general sequence and character of the work remains unchanged. The whole of the detail of the text has, however, been completely checked, revised, and brought up to date where necessary, and certain additions have been made. Thus it is felt that the time has come when the student should be introduced to simple microchemical methods, since apart from their convenience, and the economy of materials they involve, they provide valuable exercise in manipulation which no student can afford to ignore. The principal applications dealt with are simple volumetric and gravimetric methods, the micro-Kjeldahl method, micro-electrodeposition and micro-gas analysis; many of the methods do not involve the use of a micro-balance, and it has been thought best to deal with them after their "macro" counterparts, rather than in a separate microchemical section.

It was felt too that the useful nephelometric and conductometric methods are so closely allied to colorimetric and potentiometric methods, respectively, that they too should now receive some attention. Some simple examples of established value have therefore been given; they require no particularly elaborate apparatus, and are well within the resources of the ordinary laboratory and the capacity of the student. In this connection reference may also be made to the extension of the section on the colorimetric determination of  $P_H$  values to samples other than water; and to the inclusion under the same heading of the drop-ratio method, which avoids the necessity for the laborious preparation of ranges of standard buffer solutions. Another major innovation is a short note on errors and their statistical evaluation, a subject which is, rightly, attracting much attention in analytical circles; it is important that the student too should be in a position to assess to some degree the accuracy of the procedure he is using.

So far as individual determinations are concerned, the following are some of the more important of the additions. The gravimetric determination of zinc with pyridine and thiocyanate, of nitrates with nitron, and of sodium with zinc uranyl acetate; the iodide-iodate method for the volumetric standardisation of acids and its use for the correlation of standard solutions, formal titration, and sulphates by the volumetric

benzidine method. Additional colorimetric methods include the dithizone method for lead, and methods for phosphates and fluorides; it was felt too that the practical importance of the standard Gutzzeit arsenic test fully warrants its inclusion. Additions falling under the headings of general and commercial analyses include determinations of free lime, the cupron method for molybdenum now increasingly in use for steel analysis, the palmitate method for the hardness of water, and determinations of biological oxygen demand and of oxygen saturation.

Improved modifications of many of the existing methods are also given, but in all cases only methods which are both well-tried and suitable for the student have been chosen. A break with tradition is the use, where appropriate, of the description "determination" in place of "estimation," as it is felt that this is fully justified by modern custom.

A great effort has been made to keep the size of the book within reasonable limits, despite the natural tendency for it to grow as the result of the inclusion of more new matter in each edition. Slight alterations have enabled this tendency to be more than offset in the present Edition without impairing either the textual clarity or the scope of the book, or interfering with its traditional lay-out. There have been certain deletions, but only of redundant and doubtful material, and the "classical" methods have all been retained.

It is hoped that as a result of the modifications and additions outlined above, the student will continue to turn to this book for a reliable cross-section not only of the standard methods of analytical chemistry, but also of the modern trends of the subject; and that he will still find many uses for it after his analytical career has started.

J. G.

### ACKNOWLEDGMENTS

The author gratefully acknowledges assistance in connection with illustrations from the following:—

Messrs. E. Arnold & Co. (Figs. 103 and 143, from "Laboratory Handbook of Pulp and Paper Manufacture").

Messrs. F. E. Becker & Co. (Figs. 27, 64, 121).

Messrs. J. & A. Churchill Ltd. (Figs. 4, 45 and 100, from "Pregl's Quantitative Organic Microanalysis").

Messrs. A. Gallenkamp & Co. Ltd. (Figs. 14, 70, 102, 107, 142).

Messrs. Griffin & Tatlock Ltd. (Figs. 7, 63, 75, 91, 101, 115).

Messrs. L. Oertling Ltd. (Figs. 2, 3, 5).

Society of Public Analysts and other Analytical Chemists (Figs. 112, 113).

# CONTENTS

## PART I

### GENERAL PROCESSES

#### SECTION I

	PAGE
The Chemical Balance. Weights and Weighing . . . . .	1-11
Balances. Weights. Adjusting and Testing the Balance and Weights. Methods of Weighing. Directions for Weighing.	

#### SECTION II

Some Physical Determinations . . . . .	12-22
Density of Solids and Liquids. Melting-points. Boiling-points.	

#### SECTION III

General Analytical Operations . . . . .	23-58
Mechanical Preparation of Solids. Drying Methods. Solubility of Solids. Evaporation. Filtration. Drying and Ignition of Precipitates. Preparation of Pure Compounds. General Rules for Working.	

## PART II

SIMPLE GRAVIMETRIC DETERMINATIONS . . . . .	59-103
---	--------

#### SECTION IV

Errors in Gravimetric Analysis. Copper. Nickel. Cobalt. Iron. Aluminium. The Sulphate Group. Calcium and Oxalates. The Chloride Group. Lead. The Phosphate Group. The Alkali Metals. Ammonia and Nitrates. Carbon Dioxide. Water. Metals precipitated as Sulphides. Tin as Dioxide. Mercury. Silica in a Silicate. Fluoride. Boron.

## PART III

### VOLUMETRIC ANALYSIS

#### SECTION V

Introduction . . . . .	104-117
General. Volumetric Apparatus and its Calibration. Standard Solutions.	

#### SECTION VI

Alkalimetry and Acidimetry . . . . .	118-138
$P_m$ Notation. Indicators. Normal Solutions. Mixtures of Sodium Carbonate and Sodium Hydroxide, and of Sodium Carbonate and Sodium Bicarbonate. Barium. Alkali Borates. Ammonia. Nitrates by Reduction to Ammonia. Standard Barium Hydroxide. Phosphates by Molybdate Process. Other Determinations.	

#### SECTION VII

Oxidation-Reduction Reactions . . . . .	139-190
Potassium Dichromate. Oxidation-Reduction Indicators. Potassium Permanganate. Cerie Sulphate. Iodine and Potassium Iodide. Potassium Iodate Potassium Bromate. Chloramine-T. Titanous Chloride.	

## SECTION VIII

	PAGE
Unclassified Volumetric Determinations . . . . .	191-204
Sodium Chloride. Silver. Adsorption Indicators. Silver Nitrate. Potassium Cyanide. Potassium Thiocyanate. Zinc by Ferro- cyanide. Lead by Molybdate. Phosphates by Uranium Solution.	

## PART IV

## MISCELLANEOUS METHODS OF ANALYSIS

## SECTION IX

Electrometric Methods . . . . .	205-233
Measurement of pH by Indicators. Buffer Solutions. Potentio- metric Titrations. Conductometric Analysis. Electro- deposition Analysis.	
Colorimetric Analysis . . . . .	234-251
Introductory. Apparatus. Metals. Anions. Ammonia. Carbon in Steel. Arsenic. Nephelometric.	
Other Methods . . . . .	251-253
Micro-chemical, Spectrographic. Polarograph. Fluorescence Analysis.	

## PART V

## APPLIED QUANTITATIVE ANALYSIS

## SECTION X

Technical Inorganic Analysis . . . . .	254-347
The Sampling of Solids. Copper-Silver Alloy. Ores. Soda-ash. Limestone and Lime. Silicates and Glass. Zinc-blende. Galena. Copper Pyrites. Non-ferrous Alloys. Bauxite. Iron Ores. Iron and Steel. Coal and Coke. Fertilisers. Tanning Materials. Dry Assay of Ores.	

## SECTION XI

Water Analysis . . . . .	348-374
Sampling. Suspended and Dissolved Solids. Free and Saline Ammonia. Albuminoid Ammonia. Organic Matter. Determination of Chloride and Free Chlorine. Nitrites and Nitrates. Hardness. Poisonous Metals. Mineral Constituents. Dissolved Oxygen and Oxygen Demand. Discussion of Results and Analyses.	

## SECTION XII

## Analysis of Foodstuffs

Milk . . . . .	375-382
Solids. Ash. Fat. Other Principal Constituents. Discussion of Results of Analyses. Acidity. Preservatives.	
Butter . . . . .	382-390
Water. Curd. Salt. Ash. Boric Acid. Fat. Acidity. Foreign Fats. Fatty Acids. General Remarks on Adulteration of Butter.	
Beer, Wine and Spirits . . . . .	390-393
Alcohol. Original Gravity of Beer. Salt.	
Sugar . . . . .	393-399
Moisture. Ash. Glucose and Cane Sugar. Polarimetric Methods.	
Tea . . . . .	399-400
Moisture. Ash. Tannin. Theine.	

## SECTION XIII

	PAGE
<b>Examination of Oils, Fats and Waxes</b> . . . . .	401-418
Introductory Discussion. Preparation of Sample and Preliminary Analyses. Density. Melting-point. Heat of Reaction with Sulphuric Acid. Water. Acid and Saponification Values. Unsaponifiable Matter. Iodine Value. Hehner Value. Neutralisation Value. Acetyl Value. Qualitative Colour Tests for Oils. Discussion of Methods and Results.	
<b>Soap Analysis</b> . . . . .	418-421
Sampling. Moisture. Ash. Fatty Acids. Total Alkali. Matter Insoluble in Alcohol. Free Alkali. Resin. Potash Soap. Leeds Scheme.	
<b>Mineral Oils and Waxes</b> . . . . .	421-425
Preliminary Remarks. Acidity. Saponification Value. Non-Volatile Matter. Sulphur. Hard Asphalt.	
<b>Essential Oils</b> . . . . .	425-426
Solubility in Alcohol. Distillation Tests. Odour.	

## PART VI

## GENERAL ORGANIC ANALYSIS

## SECTION XIV

<b>Organic Analysis</b> . . . . .	427-445
Carbon. Hydrogen. Nitrogen. Halogen Elements. Sulphur. Phosphorus.	

## SECTION XV

<b>Determination of Molecular Weights and Vapour Densities</b> . . . . .	446-459
Equivalent Weights of Acids and Bases. Molecular Weights by Depression of Freezing-point. Molecular Weights by Elevation of Boiling-point. Vapour Density by Victor Meyer's Method. Vapour Density by Dumas' Method.	

## PART VII

## GAS ANALYSIS

## SECTION XVI

<b>Introductory</b> . . . . .	460-466
Reduction of Volumes to Normal Conditions. Calibration of Measuring-Tubes.	
<b>The Hempel Gas-Apparatus</b> . . . . .	466-477
The Apparatus and Its Use. Reagents for Absorption. Collecting a Sample of Gas. Analysis by Absorption. Analysis by Combustion.	
<b>The Lunge Nitrometer</b> . . . . .	477-482
Oxides of Nitrogen in Vitriol. Alkaline Nitrates. Gas Analysis. Compounds which Evolve Gas on Decomposition.	
<b>Mikro-Analysis of Gases</b> . . . . .	482-484
<b>Determination of Carbon Dioxide by the Pettenkofer Method</b> . . . . .	484-486

## PART VIII

## REFERENCE TABLES, ETC.

	PAGE
Errors and their Statistical Evaluation . . . . .	487-488
Results of Typical Analyses . . . . .	489-491
Ferrous Alloys. Non-ferrous Alloys. Minerals. Sulphide Ores. Miscellaneous Substances. Fuels. Lime, Mortar and Silicates. Manures.	
Tables of Useful Constants . . . . .	495-537
Buffer Solutions. $P_H$ Indicators. Density, Specific Volume and Expansion of Water. Calibration of Volumetric Apparatus. Times of Outflow for Pipettes and Burettes. Pressure of Aqueous Vapour. Alcohol Tables. Specific Gravity Tables. Characteristics of Oils, Fats and Waxes. Hydrometer and Thermometer Scales. Weights and Measures. Conversion Data. Useful Memoranda. Lists of Common Bench Reagents. Books for Reference. Factors for Gravimetric Analysis.	
Index . . . . .	539-553
Anti-logarithms . . . . .	554-555
Logarithms . . . . .	Back Cover
Atomic Weights . . . . .	Front Cover

# PART I

## GENERAL PROCESSES

### SECTION 1

#### THE CHEMICAL BALANCE. WEIGHTS AND WEIGHING

In quantitative analysis, accurate and speedy weighing must constantly be carried out. Hence it is essential that the student should become

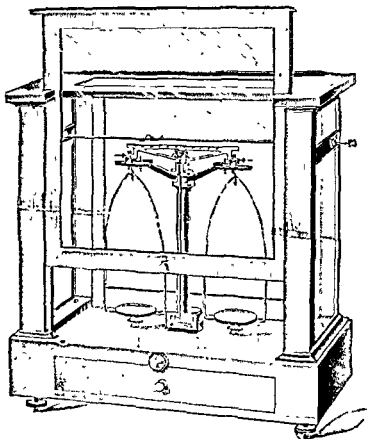


FIG. 1. THE CHEMICAL BALANCE.

familiar with the chemical balance. The commoner forms of balance and the methods of using them are described below.

#### The Balance

The Chemical Balance represented in Fig. 1 consists essentially of a rigid beam which is supported near to and slightly above its centre of gravity. From each end of the beam, and equidistant from its centre, scale-pans are suspended. In order to diminish the friction of the working parts at the points of support and of suspension, three agate knife-edges



which work upon agate planes are set in the beam. The beam and the pans are supported by these edges upon planes set in them. When the balance is not in use, the beam is lifted from the knife-edges and is supported by a T-shaped rest; the pans are also supported from beneath. Both the beam and the pans are released either by means of a disc with milled edge in the front of the balance case (as in Fig. 1), or by a handle at the side.

Attached to the bottom of the balance-case are three or more set-screws for adjusting the balance to a horizontal position. A spirit-level on the floor of the case, or a small plumb-line near the pillar, indicates when this adjustment has been correctly made.

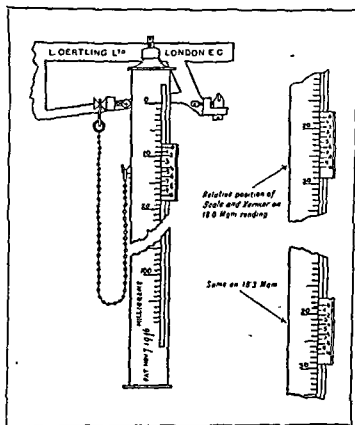


FIG. 2. CHAINOMATIC BALANCE.

The beam of the balance is commonly graduated in ten equal divisions, and a 10-milligram rider is used for weighing fractions of milligrams. The beam is, however, sometimes divided differently and riders of different weights may be used. The shorter the beam, the more rapidly will it swing.

The centre of the beam of the balance carries a long pointer which moves over a scale on the balance floor, and at the ends of the beam are brass nuts mounted on fine horizontal screws. The unloaded balance can be so adjusted by rotating these nuts that when the beam is still, the pointer is at the centre, or zero, of the scale.

The Balance is enclosed in a Glass Case provided with balanced sliding glass sashes at the front and the back, and with hinged side doors. This

case shields the balance from dust, acid fumes and moisture. It also prevents air-currents from disturbing the scale-pans during weighing. The balance should be kept in a room which is as free as possible from acid fumes and from damp, and which is not subject to great changes of temperature. As a further precaution, a jar partly filled with small pieces of calcium chloride, coloured silica gel, or soda-lime, but not with strong sulphuric acid, should stand inside the case. These absorbents must be renewed from time to time.

**The Support on which the Balance Rests** must be free from vibration. It may be a slate or stone slab, resting on pillars which are let into the foundation of the building and which are out of contact with the floor. Alternatively the slab may be isolated from the vibrations of the floor by supporting it on brackets firmly attached to the wall.

It is important that the two arms of the balance-beam are the same in length and, therefore, they must remain at the same temperature. It follows that the position of the instrument should be so chosen that it is not heated unsymmetrically either by a radiator or by sunlight; any artificial light should be so placed that it affects both arms equally.

**The Chainomatic Balance.** The general design of a balance of this type is the same as that of an ordinary chemical balance. Near to and parallel to the vertical column which supports the beam is a graduated pillar carrying a jockey and vernier scale (Fig. 2). The jockey can be made to travel up or down this pillar by turning a handle outside the balance-case. One end of a light chain is hung from the jockey and the other end is suspended from the right-hand side of the beam of the balance. The weight of the chain is therefore carried both by the beam and by the jockey. The higher the latter, the smaller the proportion of the weight carried by the beam. The left-hand side of the beam is adjusted so that when the vernier is reading zero and the balance is unloaded, the pointer swings equally about the mid-point of the balance scale. When the vernier is reading 100, with the jockey at the bottom of its run, the additional weight of the chain carried by the beam is equivalent to the weight of one decigram on the right-hand pan. The scale is so open that with the help of the vernier it can be read accurately to one part in a thousand; that is, to one-tenth of a milligram. Thus the chainomatic balance can be as accurate as one of the ordinary type. Its chief advantages are that weights less than one decigram are unnecessary, that the continual opening and shutting of the balance-case towards the end of a weighing are avoided, and that weighings can be carried out relatively rapidly.

**The Aperiodic Balance.** At the ends of the beam of this balance (Fig. 3) are two aluminium discs which move in two covered brass cups, the clearance between the discs and the cups being very small. This is in effect an air brake or damping device which causes the beam to come to rest in a short time. The period of swing can be altered within certain limits by closing or opening adjustable apertures in the discs. In another form of this balance a magnetic damping device is employed.

Further, instead of moving over a scale, the pointer itself carries a graticule which can be illuminated by an electric lamp placed at the

rear of the balance. By means of a prismatic reflecting optical system, a magnified image of this graticule is projected on to a screen of ground glass placed at the top of the balance. The graticule is ordinarily divided into 500 divisions, and with the balance in exact adjustment the image of the zero mark will coincide with a vertical line engraved on the ground-glass screen. With a load of 50 milligrams on the left-hand pan, the image of the other end of the graticule will coincide with this line. Thus one division of the scale represents one-tenth of 1 milligram.

With this balance the object is placed on the left-hand pan and the counterpoising weights on the right until the weight of the counterpoise is less than but within 0.05 gm. of that of the object. The case is then closed, the balance set swinging, and the reading of the scale taken after

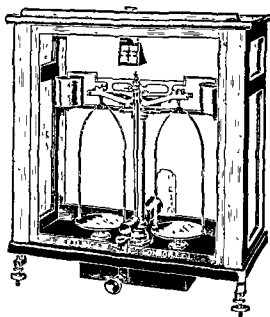


FIG. 3. APERIODIC BALANCE.

some thirty seconds. No weight smaller than 0.05 gm. is required, and no rider is necessary. The speed and accuracy of the balance, as the author can testify from personal experience, are remarkable. Even faster, though necessarily less sensitive, balances of this type are also obtainable.

With the aperiodic balance the method of weighing by swings (p. 9) is impossible, but the method of weighing by substitution (p. 9) is still available for very accurate work.

The prismatic-reflecting device is in itself a great convenience and can be fitted to the ordinary balance.

**The Microchemical Balance.** The model shown in Fig. 4 can carry up to 10 gm. on each pan, and it weighs to 0.01 milligram, or by estimation to 0.001 milligram. The beam is divided into 100 parts and carries a 5-milligram rider, and it is read by means of a magnifying glass. Another such glass enables the swing of the pointer to eliminate the effects of . . . . . and it should be remembered . . . . . (and especially of the hands) may introduce errors.

## Weights

The Metric System of weights is in almost universal use. The convenience of this decimal system is obvious.

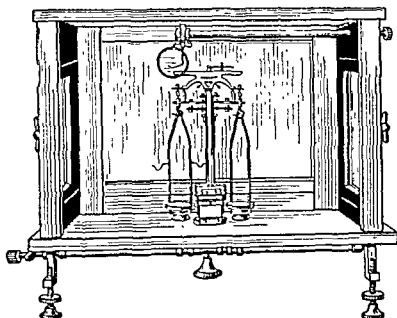


FIG. 4. MICROCHEMICAL BALANCE.

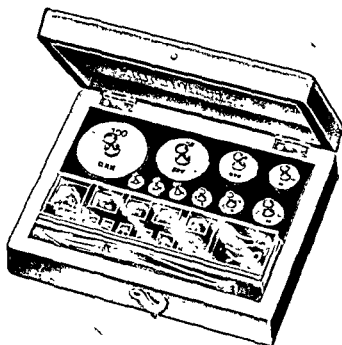


FIG. 5. BOX OF WEIGHTS.

The weights, from 1 gram, upwards, are usually made of brass (Fig. 5), and are often nickel-plated to prevent corrosion. They are cylindrical in shape, and are provided with a narrow stem, by means of which they may be lifted. The weights from 0.5 gram, downwards, are made either of

gold, platinum, or aluminium foil. The low specific gravity of aluminium renders possible the use of a greater volume of the metal, and as these weights are comparatively large and thick, they are consequently more easily handled, and are less liable to be bent or folded than those of gold or platinum. Contrary, perhaps, to expectation, aluminium weights neither gain nor lose weight over long periods, provided they are carefully handled. These smaller weights are square in shape, and usually have one corner turned up to be grasped by the forceps. It is advisable always to use forceps tipped with ivory, celluloid, or other similar material. No weight, whether large or small, must ever be touched with the fingers.

An ordinary set of weights, together with a forceps for lifting them, is shown in Fig. 5. They are contained in the usual velvet-lined box. The separate weights in sets made by different makers may differ in values.

The Rider is a piece of wire bent as is shown in Fig. 6. It is made either of gilded brass or of aluminium, and its form enables it to bestride the graduated beam of the balance and to remain on whatever part of the beam it is placed. The rider is moved from one position to another by an arm which passes through the balance-case and is operated from the outside. Milligrams and fractions of milligrams are usually registered by means of this rider.

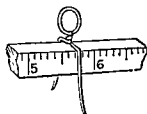


FIG. 6. RIDER ON BEAM.

Centigram riders are in common use, and riders of other weights are also employed.

When the centigram rider is used, the beam of the balance is divided into ten main equidistant graduations, each of these spaces being further subdivided into ten. Each main division therefore corresponds with a milligram, and each minor division with one-tenth of a milligram.

### Adjustment and Testing of the Balance

The balance should be adjusted and its accuracy ascertained before commencing analytical work.

#### The Balance is Adjusted as follows :

The balance and its case are first levelled by means of the levelling-screws. This adjustment is satisfactory when the bubble of air in the circular spirit-level occupies the central position.

The scale-pans and the beam are then set free from their supports in such a way that a gentle oscillatory movement is imparted to the beam of the balance. The lower end of the pointer or index attached to the beam will now swing to and fro over several divisions of the scale. If the pointer oscillates through an equal number of divisions on each side of the centre of the scale, the balance is in adjustment.

If the arcs described by the pointer on each side of the centre of the scale are of substantially different size, a further adjustment must be made by turning either of the small nuts at the end of the beam or the vane in the centre.

The observations described below are then made.

**Delicacy or Sensitiveness of the Balance.** The speed of oscillation of the pointer is noted. The slower the oscillations the greater is the sensitiveness of the balance to small differences of weight, and *vice versa*. If the sensitiveness of the balance is high, the period of oscillation will be unduly slow, and the operation of weighing will be lengthy.

The oscillations of the pointer become slower as the centre of gravity of the beam approaches more closely the axis of its suspension. Most balances therefore have a vertical screw, with a nut, attached to the central portion of the beam. By adjusting this nut, the distance between the centre of gravity and the suspension-axis of the beam can be varied at will. In this way the sensitiveness or delicacy of the balance can be changed.

When a milligram weight is placed on one of the pans of an adjusted balance and the beam is liberated, the pans should be shown to be out of equilibrium by the swings of the pointer. A delicate balance will be affected in this way by 0.1 milligram, but for many purposes it is sufficient if the balance is sensitive to 0.2 milligram.

The sensitiveness of the balance should be measured in the following way. The beam is released and allowed to oscillate, the position of the pointer on the scale at the end of each swing being noted. The scale is usually divided into 20 divisions, and it is convenient to number them from 0 to 20, beginning at the left side. The centre point, or nominal "zero," is then number 10. The mean of six swings, three to the left and three to the right, is found. The result is the true "zero" of the balance. If the difference between two successive readings to the left or right is large, it is more accurate to take the mean of seven swings, four to the left and three to the right. A milligram weight is now placed on one side of the beam and the mean of six, or seven, swings is found as before. The difference between the two means measures the sensitiveness of the balance in divisions per milligram.

The effect of increasing the load on the pans of a balance is to reduce its sensitiveness slightly. The sensitiveness for no load, 20 gm. and 50 gm. should be found, and the results entered on a slip of paper gummed to the balance-case.

**Accuracy of Construction of the Balance.** When a body is balanced against weights and the beam of the balance is set swinging and arrested several times in succession, the pointer should oscillate about the same mean position every time. Faulty construction of the knife-edges will cause differences to appear in the successive weighings.

When the pans of the balance are loaded with equal weights—say, with 50 gm.—and equilibrium is attained (if necessary, by the addition of small pieces of tinfoil to one pan), the equilibrium should be maintained when the loads are interchanged from one pan to the other. If equilibrium is not maintained when the loads are exchanged, the arms of the balance are of unequal length.

### Testing the Weights

The object of most analyses is to determine the percentage of an element in a substance. This percentage is a ratio :

$$\frac{\text{Weight of element found} \times 100}{\text{Weight of substance taken}}$$

For this reason it is frequently a matter of indifference whether or not a "one gramme" weight weighs exactly one gramme, but it is important that the ratios between the various weights are correct. If the true, absolute weights must be known it is best to calibrate against a box of weights which have been standardised in some recognised laboratory.

**Testing Weights.** Weights of the same denomination must first be marked in some way to distinguish them from each other. For example, there may be three weights of one gramme in the box. Mark them with ink 1\*, 1\*\*, 1\*\*\*. Find the zero of the balance by the method of swings. Note that the zero has probably altered slightly since you determined the sensitiveness of the balance. For the most accurate work the zero must be found daily, almost hourly, because it is always moving very slightly, through the unequal heating and cooling of the beam. Accept 1\* as standard and refer all the weights to it. Place it on the left-hand pan and weigh 1\*\* against it by the method of swings, using your sensitivity factor to calculate the apparent weight. For example, suppose the zero to be 10.25, the sensitivity factor to be 2.2 scale divisions per milligram, and 1\*\* to balance 1\*, i.e., 1 nominal gm., at 10.70. The apparent weight of 1\*\* will then be  $[1 - 0.001(10.70 - 10.25)/2.2]$  gm., or 0.9998 gm. Exchange the weights and weigh again with 1\* in the right pan. The second result will probably be different because of slight imperfections in the balance. It is sufficient to take the mean of the two results as the nominal weight of 1\*\*. The third "one gramme" weight is then standardised in exactly the same way. Next the 2-gm. weight is weighed against 1\* + 1\*\* and so on.

Then the fractional weights are standardised by weighing  $0.5 + 0.2 + 0.2 + 0.1$  against 1\*, and 0.5 against  $0.2 + 0.2 + 0.1$ , thus finding the nominal weight of 0.5, and so on. As the weights smaller than 0.01 are frequently inaccurate, it is always advisable to use the rider in their stead. A permanent record of these results should be made.

Any weight of one gramme to 50 grammes should be correct to at least one part in 2,000 in terms of the 1\* weight originally accepted as standard; any weight smaller than one gramme, to one-fifth of a milligram. If the errors are outside these limits, the weights should be adjusted by the makers.

### The Process of Weighing

There are three methods in common use for determining the weight of a substance in air—the Direct Method, the Method of Substitution, and the Method of Weighing by Swings. The result thus obtained must be corrected if the *Absolute Weight* is required.

**Direct Weighing.** In this process the substance is placed upon the left- and the counterpoising weights upon the right-hand scale-pan. The weight of the substance is assumed to be equal to the weights which counterpoise it.

The method is rapid and is in common use. Its indications are approximately correct if the balance answers satisfactorily to the tests described on p. 7, but if the arms of the beam are of unequal length, or if the balance is not in perfect adjustment, the true weight of the substance

cannot be found by this method. This is usually of no consequence in any one series of weighings, since the *differences* in weight of the substances and not their true weights are required. These differences in weight will be correctly given, provided the substances are always placed upon the same scale-pan, and provided that the condition of the balance remains unaltered between successive weighings.

**Weighing by Substitution** on any balance gives the *correct* weight of a body in air. In this method the body is counterpoised as before. It is then removed from the scale-pan, and weights are substituted for it which balance exactly those previously placed upon the other pan. The weights thus substituted for the substance will represent the true weight of the substance in air, even when the balance has not previously been adjusted to equilibrium, and when the arms are not of equal length, provided the weights themselves are correct.

Weighing by Swings has already been described. It is the most accurate, but the most tedious, of the three methods. The zero is first determined by swings. The substance is then weighed to the nearest milligram as in the direct method. The mean position of the pointer on the scale is then found and the weight calculated using the sensitivity factor. Alternatively it can be calculated by

.....htly too heavy  
.....isable to place  
.....to neglect any  
.....the substance  
.....ound, and the

mean of the two results taken.

**Absolute Weight.** Since the volume of the body weighed usually differs from that of the weights which counterpoise it, different volumes of air are displaced by the substance and by the weights. Hence a body which has been counterpoised by weights in air will not usually remain in equilibrium with the same

to the weight of the scale-pan.

### Directions for Weighing

**The Following Rules should be observed during weighing :**

1. Make sure that the scale-pans and the floor of the case are perfectly clean. If necessary, carefully cleanse the surfaces with a large camel-hair brush, which should be kept in the balance-case for the purpose. Then level the balance.
2. Gently release the pans and the beam in such a way that the beam oscillates gently. The pointer must swing through equal arcs on each side of the zero of the scale.

This preliminary adjustment is unnecessary if the weight of the substance is to be obtained by difference or by substitution. Thus, if it is required to weigh out accurately about 1 gram. of a powdered solid, the solid is put into a weighing-bottle, or into some other convenient container, and the bottle and the substance are accurately weighed together. About 1 gram. of the powder is then shaken out, and the container is again weighed. The difference between the first and second weighings will give the exact weight of the powder shaken out, because both weighings will have been subject to the same errors.



3. Examine the box of weights to make sure that all are present and in their correct places. Time can be saved by placing the box at an angle so that the turned-up corners of the smaller weights lie ready to the forceps; always lift from these corners.

4. If the operator is right-handed the substance should invariably be placed on the left-hand pan, and the weights are afterwards placed by the forceps on the right-hand pan. The weights are moved by the right hand; the beam is set free by the left.

5. The weights should be placed on the pan in systematic order. It is best to commence with a weight which is judged to be somewhat too heavy. If this is found to be the case, lower weights of the same denomination are tried in succession, until equilibrium results or the weight is somewhat too small. If the weight is too small the weights of the next lower denomination should be added to it in the same systematic order. This method will be found much speedier than that of selecting weights at random. The milligrams are usually determined by the use of the rider, and the fractions of a milligram by the method of swings.

6. The weights should be arranged on the balance-pan in an orderly way. If a comparatively heavy body is being weighed, the heaviest weight should be placed exactly on the centre of the pan and the other brass weights should be aligned with it. The decigrams and the centigrams should each be put in separate rows.

7. The case should be closed while the rider is being used, and the final observation must always be made with the case closed.

8. The weights must never be handled with the fingers, but should always be lifted with the forceps.

9. During the transfer of the weights, or the addition or removal of the body weighed, the motion of the beam and the pans should invariably be arrested. This prevents unnecessary wear on the knife-edges by violent oscillation.

Some further special precautions, which must be observed when a body is to be weighed, will be found on p. 57.

**Entry of Weight.** As soon as a weighing is completed, a careful entry of the weight of the substance should be made in the note-book. To secure accuracy write down the total value of the weights upon the pan, by noting the empty places in the box. This entry is then checked by noting the value of each weight as it is returned to its proper position in the box.

**Containers for Weighing.** Unless it is a piece of clean metal, the substance should not be placed directly on the scale-pan, but should be weighed in a suitable container. Some types of container are shown in Fig. 7. For many purposes a small test-tube stoppered with a cork will serve. Hygroscopic, efflorescent or volatile substances, and all substances which would otherwise gain or lose in weight if exposed to the air, must be weighed in closed vessels. A convenient type of stoppered weighing-bottle is shown in Fig. 7, together with a pair of thin, closely fitting glass tubes and a pair of watch-glasses, ground flat at their edges and held together by a brass spring. The tubes may be used for weighing dried filter-papers and their contents, and the watch-glasses for the determination of moisture;

for example, in coal. A pair of watch-glasses which exactly balance one another is often very useful. Not only does this avoid the trouble of counterbalancing a container when weighing out a solid; but also, where a determination has to be made in duplicate, the amount of sample weighed out on to one side can serve as the weight against which to balance the second sample when it is weighed out on the other watch-glass.

Clean pieces of metal may be weighed directly on the pan, but it must not be forgotten that this is no longer weighing by difference, and therefore that the zero of the balance must be accurately ascertained.

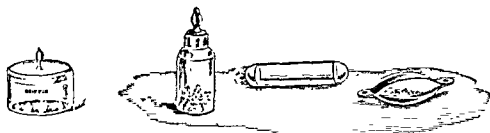


FIG. 7. VESSELS FOR WEIGHING.

If a substance is weighed while it is much warmer or colder than the air in the balance-case, it will appear to be lighter or heavier, respectively, than it really is, because the air around the hot body rises, and the current of air which flows in to take the place of that which has risen lifts the scale-pan; a body which is colder than the air, on the other hand, produces a downward air-current which depresses the pan.

Every substance tends to condense moisture from the air upon its surface; but the amount of moisture thus condensed diminishes as the temperature of the substance is raised, and increases as its temperature is reduced. A body should therefore not only be at the temperature of the air, but should have been allowed to cool in a desiccator (p. 30) if the balance is to show its true weight. For very accurate work it is necessary to standardise the time of cooling in a desiccator, *e.g.*, to 20 minutes. A tared vessel will thus cool under the same conditions when it is empty as when containing the substance whose weight is to be found by difference.

## SECTION II

### DETERMINATION OF RELATIVE DENSITY (OR SPECIFIC GRAVITY), MELTING-POINT, AND BOILING-POINT

IN connection with the chemical examination of substances it is frequently necessary to determine certain of their physical properties with precision. Processes for the determination of Relative Density (or Specific Gravity), Melting-point, and Boiling-point are described in this Section; the determination of Vapour Density will be found on pp. 454-459. The primary units of weight and volume are defined on p. 106.

#### Relative Density, or Specific Gravity

**Relative Density** may be defined as the ratio between the weights of equal volumes of two substances, one of which is taken as the standard or unit. The accepted standard for solid and liquid substances is distilled water at  $4^{\circ}\text{C}$ .

Accordingly, the relative density of a solid or liquid is obtained by dividing the weight of the substance by the weight of an equal volume of distilled water at  $4^{\circ}\text{C}$ .

Sometimes the reference weight is that of an equal volume of water at  $15.5^{\circ}\text{C}$ .

It is usually most convenient to determine the relative density at the temperature of the room, and to correct the result by the use of physical tables (p. 496).

**Specific Gravity, or Density**, is the weight of unit volume of a substance. There is no difference between the specific gravity and the relative density (referred to water at  $4^{\circ}\text{C}$ .) of a substance, because 1 ml. of pure water at  $4^{\circ}\text{C}$ . weighs 1 grm.

#### Determination of the Density of a Solid

**Solid Substances Heavier than, and Insoluble in, Water.** The substance is first weighed in air in the ordinary manner. It is then suspended from the beam of the balance by a fine fibre or by a very fine wire, preferably of platinum, and the substance is again weighed while it is immersed in cold distilled water which has previously been boiled, care being taken that its surface is free from adherent air bubbles. The temperature of the water should be near that of the room and should be carefully measured.

Air bubbles may generally be removed by brushing the surface of the solid, after it has been immersed in water, with a camel's-hair brush. In order to remove the internal air from a porous substance, however, it is necessary to immerse the substance in boiling water for some time, or to place the vessel containing the immersed substance under the receiver of an air-pump and to exhaust the air from it.

A convenient arrangement for weighing the substance in water is shown in Fig. 8. A small wooden bridge placed over the left-hand pan of the balance supports a beaker of distilled water. The suspending wire is hung

by a loop from a second hook beneath the one which supports the pan. The removal of the scale-pan, which would destroy the equilibrium of the balance, is thus unnecessary.

The density of the solid is obtained by dividing the weight of the body in air by the loss of weight which it sustains in water. Thus :

If  $W$  = Weight of solid in air,  
and  $W_1$  = Weight of solid in water,

then its specific gravity =  $\frac{W}{W - W_1}$

**Example.** In an actual experiment, a piece of brass in air weighed 16.765 grm., and in water 14.692 grm. :

Hence its relative density =

$$\frac{16.765}{16.765 - 14.692} = \frac{16.765}{2.073} = 8.088.$$

**EXPERIMENT 1.** Determine the specific gravity of a crystal of Iceland spar or calc-spar in the manner described above.

If the density is to be measured exactly, the apparent weights of the suspension wire in air and in water must be found. The latter is sometimes the greater because of surface tension effects. Corrections must also be made for the volumes of air displaced by the specimen and by the weights. It is very important that the result be stated in detail, e.g., density = 8.032 grm. per ml., the specimen being at 17° C.; or relative density = 8.032 referred to water at 1° C., the substance being at 17° C.

**Solid Substances Lighter than, and Insoluble in, Water.** The solid substance is weighed in air. It is then attached by means of a fine silk thread to a solid which is sufficiently heavy to sink it in the water. The weight of this "sinker," while it is immersed in water, is determined; and the combined weight of the solid and the sinker, while they are attached to one another and immersed in water, is also found. The density of the substance may be calculated from these data, thus :

If  $W$  = Weight of the substance in air,  
 $L$  = Its loss of weight in water,  
 $S$  = Weight of sinker in water,  
 $C$  = Combined weights of substance and sinker in water,

$$\text{then the density} = \frac{W}{L} = \frac{W}{W - (C - S)} = \frac{W}{W - C + S}$$

**Example.** A piece of paraffin-wax was found to weigh 18.45 grm. in air; the weight of the sinker in water was 49.30 grm.; the combined weights of the sinker and wax in water was 47.45 grm. :

$$\text{Hence, relative density} = \frac{18.45}{18.45 - 47.45 + 49.30} = \frac{18.45}{20.30} = 0.909.$$

**EXPERIMENT 2.** Determine the relative density of a piece of paraffin-wax, using as a sinker the piece of Iceland spar, the relative density of which was determined in Experiment 1.

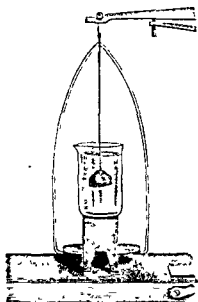


FIG. 8. WEIGHING IN WATER.

acetone, alcohol and ether in succession may be used. This is slightly quicker, but many samples of ether leave a thin film of grease on the glass.

The bottle must now be filled to the mark with distilled water at the standard temperature. This is done conveniently by filling the bottle with distilled water, the temperature of which has not been first adjusted, and then placing it in a bath of water at the required temperature. If the temperature of the water in the bath is above the standard temperature, it may be reduced by means of ice, or by dissolving some solid ammonium chloride in it.

As soon as the distilled water in the bottle has assumed the standard temperature, which may take from twenty to thirty minutes, the excess of liquid is removed by a pipette, until the meniscus just touches the mark. The dry stopper is then inserted and the bottle is quickly but carefully dried with a clean dry cloth. The bottle and its contents are weighed. The difference between the weights of the bottle, when filled and when empty, gives the weight of the water which it contains when it is exactly filled up to the mark. This weight must be carefully entered in the notebook.

The mark must be in weight with  
 sufficient lead shot,  
 until it exactly counterpoises the dry, empty bottle.

A precisely similar series of operations is now carried out with the liquid whose specific gravity is to be found. The weight of the liquid which fills the bottle to the mark is thus determined. By dividing this weight by the weight of the equal volume of water, already obtained, the relative density of the liquid can be found and the specific gravity can be calculated as shown below.

**Example.** In the determination of the density of a sample of methylated spirit, a 50-grm. specific-gravity bottle weighed, when empty, 24.5655 gm. When filled with distilled water at 15.5° C. it weighed 74.5445 gm.; and when filled with methylated spirit at 15.5° C. it weighed 65.9260 gm.:

$$\text{Hence the relative density} = \frac{65.9260 - 24.5655}{74.5445 - 24.5655} = \frac{41.3605}{49.9790} = 0.8275.$$

But from the table on p. 496, the density of water at 15.5° C. is 0.9990 gm. per ml.

Hence the density of the spirit is

$$0.8275 \times 0.9990 = 0.8267 \text{ gm. per ml.}$$

$$\text{or } \frac{0.8267}{1.000027} = 0.8268 \text{ gm. per c.c.}$$

**Another Form of Specific Gravity Bottle** which is suitable for non-volatile liquids is shown in Fig. 10. The neck of this bottle is fitted with a perforated stopper. The perforation enables the bottle to be filled completely with the liquid, to the entire exclusion of air bubbles.

After the bottle has been filled and the liquid has been brought to the requisite temperature, the stopper is dropped into the neck; the liquid will then entirely fill the bottle and the perforation in the stopper, and a small quantity will overflow from the perforation. The bottle is then wiped dry and weighed.

A cloth may be used for wiping the surface of the bottle, but the top of the stopper should be wiped by the hand, since the porous cloth would absorb some of the liquid in the capillary bore and lower the level of the liquid.

This form of bottle is widely used, but it gives accurate results only if the insertion of the stopper is always carried out with the same degree of pressure.

The **Pyknometer or Sprengel Tube** is more convenient than the ordinary specific-gravity bottle for the determination of the specific gravity of a liquid at a temperature differing from that of the atmosphere.

The pyknometer is a wide glass tube into which two thick-walled capillary tubes are fused (Fig. 11). The two capillary tubes are drawn out to slightly tapering ends, and are bent at right angles, as is shown at *a*, *b*, and a mark is lightly scratched on the tube at *b*.

The ends of the capillary tubes are ground to fit small round glass caps; these are used for covering the ends, as is shown in the figure, to prevent the evaporation of a volatile liquid after it has been introduced into the tube. With the modified form of pyknometer (p. 18) these caps are often unnecessary. The weight of the empty tube after thorough cleaning and drying is found.

The caps are then removed, and the tube is filled with distilled water by immersing the unmarked end (*a*) in water, and applying suction at the other end (*b*). The water should reach beyond the mark on the tube (*b*).

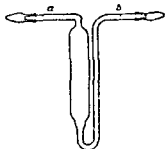
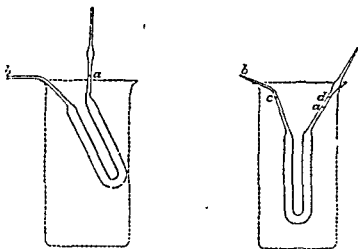


FIG. 11. PYKNOMETER.

FIG. 10.  
DENSITY  
BOTTLE.

FIGS. 12, 13. MODIFIED PYKNOMETER.

The tube and its contents are then brought to the required temperature by hanging the broad part of the tube in a beaker of water which is at that temperature (Figs. 12, 13).

The distilled water should still reach the mark on the narrow tube (*b*). If it extends beyond this mark, some water is sucked out by pressing a piece of filter-paper gently against the pointed extremity (*a*): as soon

as the liquid exactly reaches the mark, the filter-paper is withdrawn. The tube, which is now filled exactly to the mark, is removed from the water, the caps are replaced, and the whole is carefully dried and weighed. The tube is then emptied and dried, and is filled to the mark in the way already described, with the liquid whose density is required. It is again weighed.

The calculation of the density is made as indicated in the preceding example.

**EXPERIMENT 5.** Determine the density of a sample of petroleum by the specific-gravity bottle, and check the determination by means of the pycnometer.

A Useful Modification of the Sprengel Tube is shown in Figs. 12 and 13. It is especially convenient for dealing with volatile liquids and for determining the specific gravity of a liquid at temperatures much lower or higher than that of the room.

The narrow tubes in which the U-tube terminates are bent into directions nearly at right angles to one another; but each of them forms an obtuse angle with the limb of the U-tube. The tube (a), on which the mark is made for registering the constant volume, is expanded into a bulb just beyond this mark: this bulb allows expansion of the liquid to take place when the temperature rises, without loss of the liquid occurring by overflow from the end of the tube. The tube (b) must be drawn out to a tapering point to prevent the liquid from receding from this end.

In using the apparatus, the liquid is sucked in until it fills the tube and part of the bulb, and it is then brought to the desired temperature in the usual way by immersion in water. The volume of the liquid is finally adjusted to the mark by holding the apparatus with the capillary (b) horizontal (Fig. 12), and sucking out the liquid by applying filter-paper to (b) until the liquid descends to the

an erect position (b), and ascends withdrawn from the ends of the capillary tubes, and is therefore protected against loss by evaporation during weighing.

The Hydrometer is used for the rapid determination of the density of a liquid. It is a glass or metal float (Fig. 14), which is so weighted below that it assumes a vertical position when it is placed in the liquid whose specific gravity is to be determined. The stem is so graduated that the number which is level with the surface of the liquid, when the hydrometer is floating freely, shows the specific gravity of the liquid. The temperature of the liquid must be adjusted to the temperature at which the hydrometer has been graduated, which is usually  $15.5^{\circ}\text{C}$ .

The accuracy of the graduation may be ascertained by floating the hydrometer in liquids, whose densities have been determined by accurate weighing. The hydrometer may be graduated in degrees Twaddell (p. 518), or in grammes per cubic centimetre.

### Determination of Melting-points

Two methods for the determination of melting-points are described in the succeeding paragraphs. The second method is useful in special cases only.



FIG. 14.  
HYDROMETER.

**First Method.** The substance is placed in a thin-walled glass tube, which is about 1 mm. in diameter, and is sealed at one end (Fig. 15). Such tubes are easily made by softening a thin-walled narrow test-tube in the Bunsen flame, and drawing it out until it is reduced to the required diameter. The long tube thus produced is cut into tubes 5 cm. in length, each of which is then closed at one end by fusion in the flame.

The open end of one of these tubes is dipped into the finely-powdered substance in a watch-glass, so as to take up some of the powder. The tube is then held mouth upwards and stroked gently with a file or with the milled edge of a coin until the powder is shaken down to the bottom. A common mistake is to take too much of the substance; a column 2 mm. high is sufficient.

The tube is then attached to the stem of a delicate thermometer. It is generally held by surface tension alone to the wet bulb of the thermometer, but if necessary its upper end may be bound to the thermometer stem by

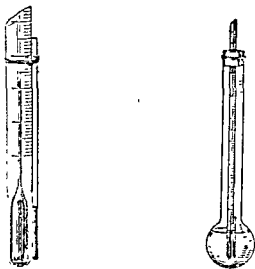


FIG. 15. MELTING-POINT APPARATUS.

a turn or two of fine copper wire. It is essential that the part of tube containing the substance should be in actual contact with the glass of the thermometer bulb.

The thermometer and tube are now placed in the Kjeldahl flask shown in Fig. 15. This flask should be about 15 cm. long with a diameter of 3 cm. The bulb should be 5 cm. in diameter. The stem of the thermometer is held in position by a cork in the mouth of the flask, the cork having a groove cut into it to permit the escape of hot air. Alternatively, a small beaker may be used, and this gives reliable results if a small circular glass stirrer surrounds the thermometer bulb.

If the melting-point of the substance under examination is less than about  $220^{\circ}\text{C}$ ., the most suitable liquid to put in the bulb-tube is ordinary medicinal paraffin. This liquid is difficult to ignite and, as it has a low specific heat, it will not cause a very severe burn if spilt on the hands when hot. For melting-points up to about  $300^{\circ}\text{C}$ . concentrated sulphuric acid may be used. A crystal of potassium nitrate added to this will prevent darkening by charring, but when working at the highest temperatures it is important that the sulphuric acid be pure and fresh.



The naked bulb is heated by a small, moving, cool flame, and the melting-point is observed. It is often best to carry out the first experiment rapidly, and to check the result by repeating the fusion, using a *new tube containing a fresh sample of the substance*, since re-fusion often takes place at a lower temperature. It is quicker to carry out a first experiment with a fast rate of heating and a second at a slow rate through the range near the melting-point than to carry out one only, slowly through the whole range.

If the Mercury Thread of the Thermometer extends above the surface of the liquid when the melting-point is read, a correction must be applied for the contraction due to the cooling of the mercury.

The following formula gives the correction to be added :

$$N(T - t) \times 0.000143.$$

Here  $N$  stands for the number of degrees on the thermometer stem which are not heated by the liquid ;  $T$  (in  $^{\circ}\text{C}.$ ) is the temperature indicated by the thermometer ;  $t$  is the temperature read on a second similar thermometer the bulb of which is placed midway between the surface of the liquid and the top of the mercury column at a point 10 cm. on one side of the latter, and shielded from the source of heat ; and 0.000143 is the apparent coefficient of expansion of mercury in glass.

**EXPERIMENT 6.** Determine the melting-point of sulphur or of benzoic acid in the apparatus shown in Fig. 15, using medicinal paraffin in the bath.

**Second Method.** The substance, in the form of powder, of minute crystals, or of thin slices, is held between two microscope-slide cover-glasses. This makes the exact moment of fusion very evident, because the film of substance, which is more or less opaque before it is melted, becomes suddenly transparent because of the large heating surface exposed, relative to the amount of substance used.

small quantity  
of a very thin

ape shown in  
then cutting  
necessary, the

holder and the glasses may be more firmly bound together by means of thin platinum wire.

The whole is now suspended in a wide test-tube in contact with the bulb of a thermometer. The test-tube serves as an air-bath, and is immersed nearly up to its mouth in a bath

In order to prevent undue convection of air, it is as well to

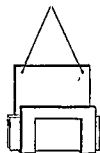


FIG. 16.  
MELTING-POINT  
APPARATUS.

### Determination of Boiling-points

The Boiling-Point of a Pure Liquid is the temperature at which the vapour pressure of the liquid is equal to that of the atmosphere ; it is always the same if the liquid is boiling under the same pressure. The boiling-point is therefore frequently used to test the purity of a liquid, as well as to identify it. Two methods are described. The first is most commonly employed ; the other is a micro-method.

**First Method.** The liquid is placed in a flask (Fig. 17), the neck of which

has a delivery tube in the side, and is closed by a stopper, through which a thermometer passes.

The liquid is gradually heated until it boils, the side-tube serving to carry away the vapour which is produced. The thermometer should be so placed that the top of the bulb is just level with the centre of the side-arm of the distillation-flask. The bulb and part of the stem of the thermometer are thus constantly surrounded by the vapour of the boiling liquid. If the liquid becomes superheated it will bump; this may be prevented by adding two or three small pieces of clean porous plate. If the boiling-point of the liquid is above  $120^{\circ}\text{C}$ ., an air condenser, consisting of a long glass tube slipped over the side-tube of the flask, will suffice for condensing the vapour. If the boiling-point is below  $120^{\circ}$ , a Liebig or other form of cold-water condenser should be used. As soon as the reading of the thermometer remains constant, the temperature registered is the boiling-

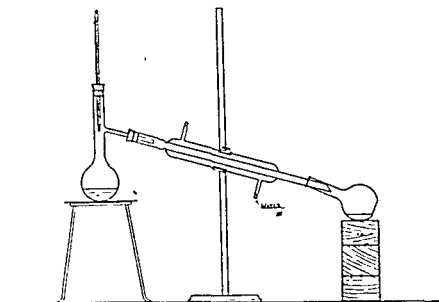


FIG. 17. BOILING-POINT APPARATUS.

point of the liquid. This reading will, however, require correction by the formula given on p. 20, if the upper part of the thread of mercury extends above the cork.

It should be remembered that any considerable change in the atmospheric pressure will cause an appreciable variation in the boiling-point. It is therefore necessary to specify the barometric pressure at the time of the experiment. Thus, if the boiling-point observed is  $62^{\circ}\text{C}$ . and the barometric pressure is 760 mm., it may be entered:  $62^{\circ}\text{C}/760\text{ mm}$ . An approximate correction may be applied, if necessary, on the assumption that an increase or diminution of 20 mm. in the atmospheric pressure from 760 mm. causes an increase or diminution in the boiling-point of approximately  $1^{\circ}\text{C}$ ., respectively.

**EXPERIMENT 7.** Determine the boiling-point of aniline, using an air condenser; and of chloroform, using a Liebig condenser.

**Micro-Method.** This method may be employed when only a small quantity of liquid is available; its error is usually  $1^{\circ}\text{C}$ .

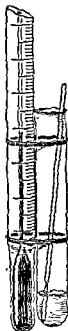


FIG. 18.  
BOILING-POINT  
APPARATUS.

About 1 ml. of the liquid is placed in a thin-walled test-tube, about 8 cm. long and 1 cm. in diameter. The test-tube is fastened to the thermometer by means of fine wire, as is shown in Fig. 18. A fine open capillary tube of thin glass, a little more than 8 cm. in length, is then prepared by heating the walls about 1 cm. from one end in the tip of the flame for a second, so as just to fuse them together; the tube is placed in the test-tube as is shown in the figure.

The apparatus is now dipped into a vessel containing some suitable liquid, with the mouth of the test-tube projecting above its surface. When the vessel is heated, small bubbles of air will slowly escape from the lower end of the capillary tube. As the temperature gradually rises, the evolution of bubbles of vapour will eventually become rapid and continuous, indicating that the liquid has reached its boiling-point. The temperature is then read. The determination should be confirmed by repeating the process with a new capillary tube, and fresh liquid.

EXPERIMENT 8. Determine the boiling-point of a sample of benzene by the above method.

## SECTION III

**MECHANICAL PREPARATION OF SOLIDS. DRYING OR DESICCATION. SOLUTION, EVAPORATION. PRECIPITATION, FILTRATION. TREATMENT OF PRECIPITATES. PREPARATION OF PURE SUBSTANCES AND OF DOUBLE SALTS. GENERAL RULES FOR WORKING.**

### Mechanical Preparation of Solids

Before commencing the Analysis of a Substance, attention must be paid to the following points :

1. The specimen chosen for analysis must be a fair and average sample of the material under examination.

2. The substance, if a solid, must almost invariably be in a finely-divided state.

**Sampling.** As sampling is by no means easy and as it can be most suitably discussed in connection with the analysis of ores and minerals, it is described later (p. 254). The analyses described in Parts II. and III. of this book deal mostly with materials which are homogeneous and which need not therefore be sampled specially.

**Powdering.** The second condition, that the solid substance to be analysed must be in a very fine state of division, is also usually essential, because a substance is then most readily dissolved by solvents or by fluxes. The substance is usually powdered in a mortar. It is essential that the material and surface of the mortar are such that the powder will be contaminated neither by abrasion of the mortar nor by brittle fragments which have chipped off. For salts and other comparatively soft substances, a porcelain or a Wedgwood mortar may be used ; but for many minerals and hard materials generally, a mortar of steel or of agate is necessary.

In reducing a mineral to powder, the large pieces may first be broken by placing them on a square steel anvil, surrounded by a shield of tin-plate and by striking them with a hammer. The smaller pieces thus produced are then reduced to coarse powder, either in a steel mortar of the usual shape, or in a steel percussion mortar (Fig. 10), which consists of a hollow cylinder fitting into a depression in the base. The substance is placed in the cavity thus formed. The solid cylindrical pestle is then pushed down upon the substance, and is struck repeatedly with a hammer until the substance is powdered.

The coarsely-powdered substance is next introduced, in small portions at a time, into an agate mortar, and the substance is further powdered by

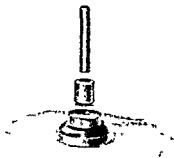


FIG. 10. STEEL MORTAR.

trituration, *not by blows*, until it forms an impalpable powder. When the powder is sufficiently fine, it will feel smooth when it is worked with the pestle. Hand-mills suitable for reducing hard materials to coarse powder can be obtained.

**Sieving.** To make certain that the substance is sufficiently finely powdered, it is advisable to sift it. If a sieve is used it is important to pass *all* the substance through it, because those harder parts of the material which are the more difficult to powder will probably differ from the rest in composition. The type of sieve recommended for this purpose has been specified by the British Standards Institution, and is known as the British Standard sieve. These sieves can be obtained in a large number of different sizes, the sieve number being the number of meshes to the linear inch. Thus sieve No. 100 is woven from phosphor-bronze wire of diameter 0.004 inch (0.102 mm.) in such a way that there are 100 strands to the linear inch. The apertures are square and the length of the side of each hole will therefore be 0.006 inch (0.152 mm.). The screening areas of most of these sieves are about 36 per cent. The finest sieve in this set is No. 300, with square holes of side length 0.0021 inch (0.053 mm.), and the coarsest is No. 5, with holes of side length 0.132 inch (3.35 mm.). The sizes of the sieves are based on a ratio of approximately  $\frac{6}{5}$  between linear aperture measurements of consecutive sieves. Thus the next finest to

No. 100 should have apertures of side length  $\frac{0.006 \times 5}{6} = 0.005$  inch.

As this would entail drawing the wire to a special size, a side length of 0.0049 inch is adopted. This involves the use of a wire of diameter 0.0034 inch, giving 120 strands to the linear inch. The sieve is therefore known as No. 120.

The screens should be mounted in frames of circular cross-section and diameter 8 inches, in such a way that for sizes finer than 120 the screen should be 2 inches below the top of the frame, and for sizes coarser than 120 the depth should be 1.5 inch. All the joints in the frames should be soldered, and the frames themselves should not be japanned. For sizes finer than No. 40, the wire of the screen should be of phosphor-bronze; for coarser sizes, of steel.

There are also two other sets of British Standard sieves. The intermediate sieves are made of steel wire and are known by the size of their apertures, which increase by increments which are simple fractions of inches. The screens of the coarsest set are perforated metal plates. The plates are 0.063 inch (1.6 mm.) in thickness and are mounted in frames 18 inches in diameter. The holes are square and of square pitch. These screens have a comparatively large screening area. Thus the  $\frac{1}{2}$ -inch plate has a screening area of 52 per cent.

There is, unfortunately, a second set of sieves which is much used, as it has been standardised by the Institution of Mining and Metallurgy (I.M.M. sieves). These closely resemble the British Standard series, except that their sizes are slightly different, the general principle being that the side length of the aperture should be the same as the diameter of the wire. The size number is again the number of strands to the linear inch. Thus I.M.M. No. 100 will have 100 strands of diameter 0.005 inch to the linear inch and the side length of the aperture will also be 0.005 inch, giving a

screening area of 25 per cent. It will be seen that the holes in I.M.M. No. 100 and B.S. No. 120 are of approximately the same size, but that the screening area of the latter is considerably larger than that of the former. Similar relationships between the sieve numbers hold good throughout the two sets.

### Drying, or Desiccation

Many Substances contain Water of combination, as, for example, water of crystallisation. They may also be damp. Sometimes it is difficult to draw a hard-and-fast line between combination, adsorption of water and mere wetness. In some technical analyses the substance must be analysed "as received" and without preliminary treatment; in others it must undergo an agreed drying process. A compound used as a standard in analysis must be of definite composition. Many such compounds are hydrates. They must contain neither too much water nor too little, and must therefore be dried under carefully-controlled conditions. Different methods of drying must be adopted to suit each individual case. Some of these methods and the apparatus used are described in the following paragraphs.

**Drying at Ordinary Temperature and in Vacuo.** If a solid is to be dried at room temperature, as, for example, in removing the adherent mother-liquor from crystals, a convenient method is as follows:

The moist solid, after draining in a Buchner funnel (p. 54), is placed in a thin layer on a porous tile or plate to drain further. After several hours, when most of the moisture will have disappeared, thin layers of the substance are pressed between folded sheets of filter-paper. The paper is renewed until the sheets no longer become moist. Most of the adherent moisture will then have been removed. The use of filter-paper in certain cases may be unnecessary, as drying may be completed in a desiccator as described below.

If the substance is a liquid, or if it decomposes when heated, it may be dried by placing it in a desiccator, preferably of the vacuum type, and exposing it to the drying action of sulphuric acid or of some other absorbent of moisture.

**Drying at Steam-heat.** The substance is more rapidly dried by heating a thin layer on a watch-glass or in a shallow flat-bottomed dish (Fig. 7, p. 11), in a gentle current of air in a steam-oven (Fig. 20), or in the special apparatus described on p. 29.

The steam-oven is usually made of copper, and has double walls; the door may be glazed to give a view of the interior. The casing of the oven is filled to about one-third of its height with water. Heat is then applied by means of a Bunsen or other burner. When the water boils, the upper part of the hollow casing becomes filled with steam, and the temperature of the interior of the oven approaches 100° C.; the steam is either allowed to blow off into the air, or is condensed by a long tube or condenser and returned as water to the oven.

A gentle current of air passes through the oven when it is heated, entering through an inlet near the bottom of the door and escaping from an outlet in the top by convection.

It has been found possible to attain a higher temperature than that usually recorded in a steam-oven by substituting a narrow copper tube for the usual inlet for air through the door. In Fig. 20 one end of the tube is seen immediately beneath the door, and the other end opens into the oven flush with its bottom. The pipe itself is thus constantly surrounded with boiling water, and the air passing through it into the oven enters at a temperature of nearly  $100^{\circ}\text{C}$ . There is a small air outlet provided at the upper part of the back of the oven.

The arrangement for ensuring a uniform level of water in the steam-oven will be understood from the sectional drawing (Fig. 21). A constant supply of cold water flows into the vessel which is attached to the side of

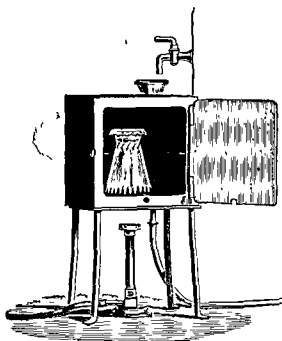


FIG. 20. WATER-OVEN.

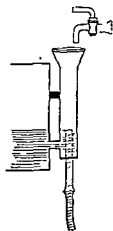


FIG. 21. WATER-SUPPLY  
(SECTION).

the steam-oven, and the excess flows away by the central tube to a sink. The water in the bath is maintained level with the top of this overflow tube through a small connecting tube below.

The heating of steam-ovens may be advantageously combined with the distillation of water. An apparatus suitable for this purpose is represented in Fig. 22: it may stand conveniently in a recess in the laboratory wall and under a glazed projecting hood, to obtain a good upward draught.

The boiler forms the bottom of the steam-oven casing, and is heated by a powerful longitudinal burner. The steam issuing from this boiler, passes between and round the various ovens, and is condensed in a special condenser which is seen above the steam-oven and is described below. The condensed water flows into a store-jar down the pipe shown to the left of the figure. The overflow condensing water is taken away by the tube shown on the right.

The condenser is made of copper, thickly tinned inside. It is very

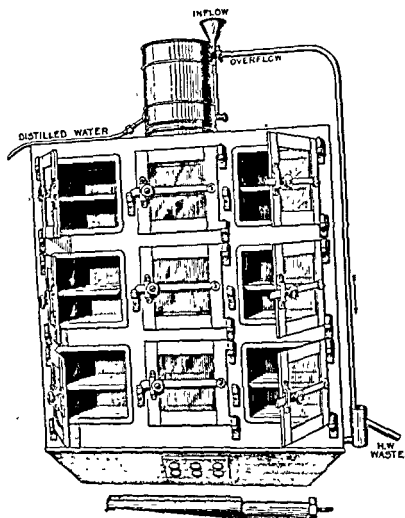


FIG. 22. STEAM-OVENS AND STILL.

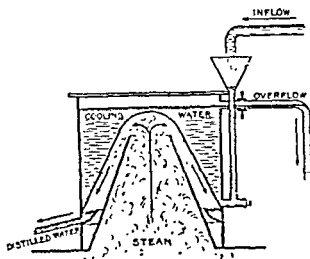


FIG. 23. THE BROWN CONDENSER.



efficient and is readily cleaned. Its general construction is seen in the sectional drawing (Fig. 23). The steam enters through a wide bottom opening and impinges upon the lower surface of the dome, which is kept cool by contact with the constantly-renewed cold water on its upper surface. The distilled water formed by condensed steam is collected in an annular internal channel, from the bottom of which it flows through a tube to the storage-jars. Since all the connections are made by screw-union joints, the parts of the apparatus can easily be disconnected for cleaning and repair.

The apparatus will run uninterruptedly, without attention, after suitable regulation of the supply of gas and condenser water.

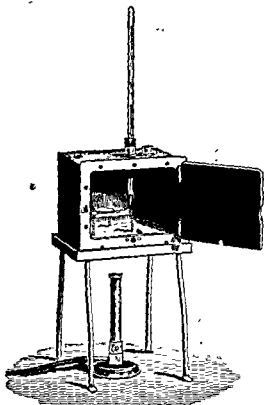


FIG. 24. THE HOT-AIR OVEN.

**Drying at above 100° C.** An air-oven (Fig. 24) is usually employed, the construction of which is almost identical with that of the water-oven, except that the external walls are frequently made of Uralite instead of copper. Air, heated to the necessary temperature, takes the place of boiling water and steam in the jacket.

Since the walls of the oven are usually much hotter than the inside air, the substance to be dried must not be in contact with the oven. A pipe-clay or silica triangle with the wire ends turned down at right angles to the plane of the triangle, or the support for an inverted gas mantle, makes a convenient stand for the substance and keeps it from touching the oven; or a square plate of porcelain or of Vitreosil, slightly less in size than the bottom of the oven, may be supported about  $\frac{1}{2}$  inch above the floor.

A thermometer passes through a bung in the top of the oven, and registers the temperature of the interior. Any temperature required can be obtained by suitably regulating the gas supply. In many ovens the temperature throughout is not uniform. It is therefore necessary when it is inadvisable to heat a substance other than at the exact temperature specified, to see that the bulb of the thermometer is close to the dish containing the substance. It will be found that, when once the flame has been properly regulated, the temperature will remain fairly constant for several hours if a gas-governor has been introduced into the gas service-pipe. Gas-regulators are also sold by instrument makers for insertion into the oven, and these will maintain a constant temperature.

Electrically-heated ovens, with wide ranges of temperature, are now available. They may be connected up with the ordinary electric lighting supply, and can be closely controlled by a rheostat.

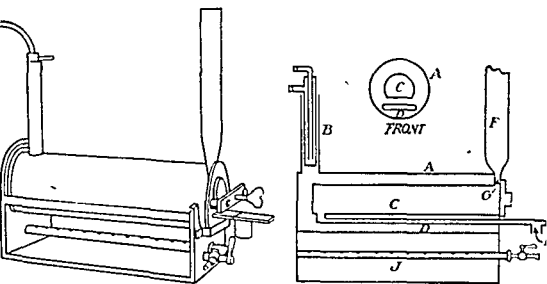


FIG. 25. OVEN FOR DRYING AT CONSTANT TEMPERATURE.

**Oven for Drying at a Constant Temperature.** In this oven the substance to be dried is exposed with certainty to the desired temperature while a current of air or other gas, either in the ordinary or dried condition and maintained at the desired temperature, is passing over it. This temperature is attained by completely surrounding the drying-vessel with the vapour of a liquid of suitable boiling-point, and with the liquid itself.

A muffle-shaped copper drying-chamber (C, Fig. 25), for containing the substances to be dried, is supported horizontally in a round, copper jacket (A), the space between the chamber and the jacket being partly filled with the liquid of the desired boiling-point. The liquid is maintained at its boiling-point by a series of gas-jets from a gas burner (J) beneath the jacket. The vapour of the boiling liquid is constantly condensed by the arrangement shown at (B) and returned to the jacket.

The admission of air to the interior of the drying-chamber takes place at (H) through a flat copper tube (D) which passes through the boiling liquid or its vapour without touching the jacket, and opens at (G) into the further end of the drying-chamber; the exit of the air is through a copper

chimney (F) let into the front end of the drying-chamber above the door by which the substances are introduced. If the ordinary air used (H) is left open to the atmosphere, but, by making suitable connections to it, dried air or other gases can be passed over the substance to be dried. If the oven is properly constructed the temperature throughout the chamber will be uniform.

Convenient dimensions for the apparatus are as follows: external measurement of jacket, 35 cm. long and 11 cm. in diameter; the drying-chamber is 6 cm. across at the bottom and 4 cm. high, with greatest diameter of 6.3 cm.; the height of the chimney is 27.5 cm.

The substances to be dried are conveniently ranged along a copper tray, which is too short to block the air-inlet, and the tray is then pushed into the chamber. Six watch-glasses or flat moisture-dishes can be placed on such a tray at one time.

**The Desiccator.** Substances which are too unstable to be dried by heat must be dried more slowly by exposure at ordinary temperature to a dry atmosphere, or to drying agents *in vacuo*. For this purpose the desiccators shown in Figs. 26 and 27 may be used.



FIG. 26. DESICCATOR.

Desiccators must also be used to store substances which are hygroscopic and absorb moisture from the air after they have been dried at higher temperatures. They are thus protected from contact with the moist atmosphere while they are cooling, before weighing. Apparatus which is temporarily out of use, but

which is soon to be weighed, can also be kept dry in a desiccator.

The desiccator is an air-tight vessel, the air in which is kept dry by a drying agent. Sulphuric acid, fused or granular calcium chloride and phosphorus pentoxide are the drying agents in common use. Of these, the pentoxide is the most and the calcium chloride the least efficient.

Magnesium perchlorate has recently been shown to be almost as efficient a desiccating agent as phosphorus pentoxide; its moisture absorption capacity is more than 30 per cent. of its own weight. It has the additional advantages that it remains porous, and, therefore, is particularly useful for gas-drying U-tubes (p. 87); and that it is clean and convenient to handle, and can be regenerated by heating at 200° C. for 10 hours.

The usual small, portable desiccator (Fig. 26) consists of a broad glass jar which is contracted in the middle. The lower part contains the desiccating agent; the upper, the body to be weighed. A circular piece of perforated zinc forms a bottom to the upper chamber, and on this a pipe-clay triangle, an inverted gas mantle holder, or other support for the vessel is laid. A flat lid is ground to fit accurately on the upper ground rim of the desiccator; and this rim is lightly greased, so that the fit may be air-tight.

**Drying in Vacuo.** Many substances can be completely dried by exposing them *in vacuo* in the presence of some agent which absorbs the water

vapour evolved. This method of drying *in vacuo* is also suitable for substances which decompose when they are heated. Substances which have been thoroughly dried may be kept for any length of time in a vacuum desiccator without undergoing any increase in weight.

A convenient form of desiccator for drying *in vacuo* is shown in Fig. 27. The upper portion is removable and fits closely on the lower portion. The joint is of ground glass and is rendered airtight by carefully greasing the ground surfaces. The drying agent is contained in the lower portion of the desiccator. This agent is commonly either sulphuric acid or phosphorus pentoxide. If sulphuric acid is used, it is often convenient to soak pieces of pumice stone in the liquid; if phosphorus pentoxide, the solid should be sprinkled on glass wool to increase the effective drying area.

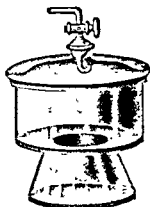


FIG. 27. VACUUM DESICCATOR.

The cover of the desiccator contains a tubulated stopper, the upper portion of which is extended into a tube for connection with a Hyvac pump, an efficient water-pump, or some other arrangement for obtaining a good vacuum. The other end of this stopper is often bent upwards in the form of a hook, from which apparatus can be hung. The real purpose of this bend is to deflect and break up the stream of air which enters the evacuated chamber when the cock is opened. If this stream is directed straight downwards it might blow away the dried substance. There are many other designs of vacuum desiccator.

### Dissolution of Solids

It is always desirable and sometimes essential that the solid to be dissolved, even though it may be classed as a very soluble substance, should be in a fine state of division; then it dissolves more rapidly. If the solid, or part of it, is practically insoluble, much time can be saved by reducing it first to an impalpable powder.

A Substance which is Soluble in Water is mixed with distilled water in a beaker, which is then placed on wire gauze over a Bunsen flame (Fig. 28). The water and powder should be stirred with a glass rod. In order to prevent loss of solution by spirting during effervescence or boiling, the beaker should be covered with a clock-glass,

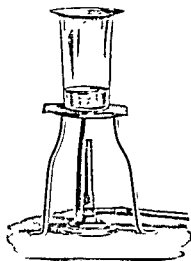


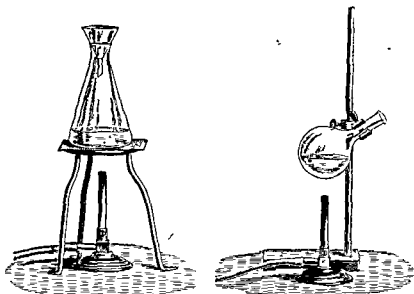
FIG. 28. DISSOLUTION OF A SOLID.

which may rest on three little U-rods of glass hanging on the edge of the beaker.

If the Liquid is Boiled, or if Effervescence occurs, as is frequently the case during solution in acids, one of the following methods may be substituted for that described above.

(a) The substance is placed in a conical flask. The solvent is added through a small glass funnel (Fig. 29), which is left in the mouth of the flask and serves to close it partially. The loss of the liquid by spirting is thus prevented, but the escape of gas is not hindered. If a conical flask is used, the mouth should never be covered with a watch-glass. The escaping gas causes the glass to rattle up and down and blows any liquid which may be condensed on it out of the vessel.

(b) The substance may be placed in a round flask, which is tilted at an angle of about  $45^\circ$  (Fig. 30). In this case the drops, thrown up by effer-



FIGS. 29, 30. DISSOLUTION OF A SOLID.

vescence or by ebullition, will be retained by striking the inside of the flask, while gas will escape freely.

**Insoluble Substances.** A process for the decomposition and dissolution of many substances which are insoluble in water and in acids is described on p. 67.

**Material of Vessels used for Solutions.** Care must be exercised in selecting vessels which will not be attacked by the solvent during solution and evaporation. Glass, silica, porcelain, and in certain cases platinum vessels may be used for acid liquids. Porcelain, silver, and nickel vessels may be used for alkaline liquids; glass vessels are less suitable, since glass is attacked appreciably by alkaline liquids, although it should be remembered that "resistance glass" is much less affected by solvents than ordinary glass, and is usually also better able to stand sudden changes of temperature. Nevertheless, even the best quality chemical glassware will dissolve, to the extent of some 10 mgrm. per 100 ml. of solution per half hour, in a boiling, 0.5 N. solution of sodium hydroxide.

### Solubility of Solids

The Solubility of a Solid may usually be determined with accuracy by means of the following simple apparatus:

The mouth of a thin-walled, glass beaker-flask, about 250 ml. in capacity, is closed with a rubber bung in which two holes have been bored. In one of the holes is fitted a short piece of glass tube bent at right angles, the tube passing just through the bung (Fig. 31). Through the other hole passes a piece of glass tube, also bent at right angles, and long enough to reach nearly to the bottom of the vessel. The lower end of this tube is slightly contracted and is bent obliquely.

The flask is now about two-thirds filled with distilled water, and it is then immersed in a large vessel containing water. The water must be maintained, by means of a suitable regulator, at the temperature at which the solubility of the substance is to be determined. The finely-powdered solid is then introduced into the flask in quantity considerably more than sufficient to form a saturated solution.

The rubber stopper is now inserted, and the end of the shorter tube is connected by rubber tubing with a water-pump. The stream of air bubbles which is drawn by the pump through the liquid causes the solid and the water in the flask to circulate, and to produce a saturated solution. A plug of cotton wool inserted into the upper end of the longer tube will serve to filter off any dust carried in the air. The supersaturation of the solution, which may arise from the evaporation caused by the passage of the air through the solution, may be prevented by saturating the air with moisture by allowing it to bubble through a similar flask containing water and an excess of the substance under examination, before allowing it to enter the final solution.



FIG. 31.  
SOLUBILITY  
APPARATUS.

Some of the clear solution may then be weighed in a stoppered bottle (Fig. 7, p. 11), and the amount of the solid dissolved in it may be found either by evaporation or, better, by volumetric or gravimetric analysis according to the nature of the substance. When it is probable that, owing to a fall in temperature, crystals will separate in the weighing-bottle, this inconvenience may be avoided by adding a little water to the bottle before it is first weighed.

In some cases it may be necessary to filter to obtain a clear solution. This is carried out most simply by decanting some of the solution into a test-tube which is already at the chosen temperature. A firm plug of cotton wool is then steadily pressed through the solution (preheated if necessary), using a thermometer. The plug must not be pressed down so far that it will disturb any solid which may be lying at the bottom of the tube. The temperature is then read, and the filtered liquid on top of the plug is poured into the weighed weighing-bottle. Note that the temperature of a liquid in a vessel immersed in a bath will very frequently not be the same as that of the bath. It should always be checked.

Solubility measurements accurate enough for many purposes can be made by shaking the finely-powdered substance with the liquid in a test-tube stoppered by a cork or rubber bung. The test-tube is placed in a thermostat, or, if the solubility is to be determined at room temperature, in a pail of water at that temperature. The purpose of the pail of water is to hold the temperature steady (the temperature of a laboratory tends to rise rapidly after work has commenced). The test-tube and its contents

are shaken from time to time. After an hour or two the stopper is removed and the liquid filtered, using a cotton-wool plug (see above). The thermometer is then read, and a suitable quantity of the liquid transferred to the weighing-bottle.

**Example.** The method of calculating the solubility of a substance from the results of an actual experiment is given below :

	Grm.
Weight of solution + bottle . . . .	31.89
Weight of bottle . . . .	16.26
Weight of solution . . . .	<u>15.63</u>
Weight of solid + dish . . . .	22.5100
Weight of evaporating-dish . . . .	<u>21.6110</u>
Weight of solid . . . .	<u>0.8990</u>

Accordingly 0.8990 grm. of the solid has been dissolved by

$$15.63 - 0.90 = 14.73 \text{ grm. of water.}$$

Therefore the weight of the solid which would be dissolved by 100 grm. of water }  $= \frac{0.8990 \times 100}{14.73} = 6.103 \text{ grm.}$

**EXPERIMENT 9.** Weigh out some 30 grm. of finely-powdered  $\text{KClO}_3$ , and pour this into the apparatus (Fig. 31). Pour in water until the flask is about two-thirds full, and pass the current of air through the liquid for half an hour, the flask being immersed in a vessel of water kept at the required temperature. Transfer some of the liquid to a clean test-tube, which must also be at the required temperature. Filter by pushing a pad of cotton wool slowly but firmly down the tube with a glass rod. Then collect the clear solution in a weighed bottle, insert the stopper, and weigh the bottle and solution.

Now pour the solution from the bottle into a weighed porcelain dish, and rinse the bottle into the dish several times with small quantities of distilled water. Evaporate all this liquid to dryness over a water-bath in a weighed dish. Then place the dish in a steam-oven for about twenty minutes, allow it to cool in a desiccator and weigh it.

The necessary data for calculating the weight of the solid which has dissolved in 100 grm. of water have now been obtained. The calculation is illustrated above.

**EXPERIMENT 10.** A saturated solution of crystallised copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is made as directed in Fig. 10. But since copper sulphate loses a part of its water of crystallisation the salt cannot be obtained by residue and weighing it, as in the case of sodium sulphate. If, therefore, about 5 ml. of the  $\text{CuSO}_4$  solution, the Cu should therefore be completely precipitated and weighed. The weight of the precipitate of  $\text{Cu(OH)}_2$  or the copper may be found. If the weight of the precipitate is known, the weight of the solution obtained, the weight of the solid which has dissolved in 100 grm. of water can be calculated, and the percentage solubility of the salt can be found.

The accuracy of the results obtained may be checked by referring to a dictionary of chemical solubilities (see p. 520).

### Evaporation

**Evaporation by Steam.** The evaporation of a liquid is frequently carried out over boiling water on a water-bath, steam being the heating agent.

A simple form of water-bath is shown in Fig. 32. It consists of a copper vessel rather more than half-filled with water, and heated by a Bunsen

burner. The upper portion is fitted with flat sheet-copper rings of gradually diminishing diameters, and the top of the bath can thus be made to support vessels of various sizes.

Evaporation is always much more rapid if the dish is sunk as deeply as possible into the bath, as is shown in Fig. 32, than if it is merely perched on the rings, so that a large area of the dish is exposed to cooling draughts of air.

A more elaborate water-bath is shown in Fig. 33. In the upper surface of this bath there are holes of various sizes, designed to fit vessels of different dimensions. These holes, when not in use, are covered by lids, as is shown in the figure. Both forms of water-bath may conveniently be fitted with a constant water supply, such as that represented in Fig. 21 (p. 26).



FIG. 32. WATER-BATH.

When the vessel is to be weighed after evaporation on a copper water-bath it is apt to stain it. (p. 26). Glass part of a broken an inch below its

upper edge.

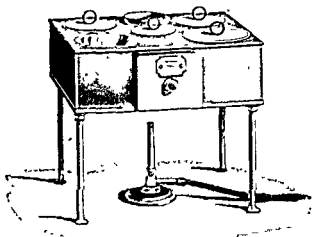


FIG. 33. WATER-BATH.

**Evaporation at Temperatures above Steam-heat.** When a temperature higher than  $100^{\circ}$  C. is required during the evaporation, one of the following methods may be used :

(a) *The Sand-bath.* The vessel containing the liquid may be placed on a sand-bath which is heated by a burner. The sand-bath is a shallow sheet-iron saucer or tray, which is covered with a layer of sand. A uniform heat can be applied to the bottom of the vessel by placing it on the sand, which is heated by a suitable burner.

(b) *The Naked Flame.* The vessel may be heated directly over a naked flame, which should be spread by a rose. In order to avoid overheating the sides of a dish above the liquid by the flame, the dish may be allowed



to rest in a circular hole in a metal or asbestos sheet; the sheet screens the upper part of the dish.

(c) *Wire Gauze, Asbestos, or Iron Plate as support.* The vessel may be supported on wire gauze, on a sheet of asbestos mill-board, or on an iron plate. This last support is a convenient source of heat for evaporating a liquid in a beaker, since the rate of evaporation can be reduced by removing the beaker to a greater distance from the part of the plate which is directly over the flame. The arrangement shown in Fig. 34 can be used, or, alternatively, a plate some 30 inches long and 15 inches wide fitted with four short legs can be placed over a large ring burner. This burner should be kept at one end of the plate, so that a considerable temperature gradient can be obtained. In all cases the iron plates should be kept thoroughly clean and coated with black lead.

(d) *The Air-bath.* Beakers may be conveniently heated in a copper air-bath. The bath is similar in shape to the water-bath represented

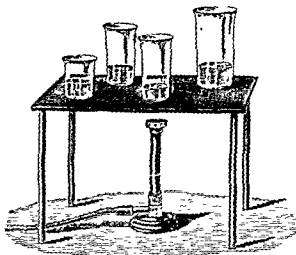


FIG. 34. EVAPORATION ON HOT PLATE.

in Fig. 32 (p. 35), but it is deeper and contains no water. The beakers are supported by their curved-over edges in the holes in the top of the bath, the holes being reduced, if necessary, by means of flat copper rings. The beakers are thus immersed in the hot air inside the bath, and are exposed to a uniform and easily regulated temperature, which can be ascertained by means of a thermometer, the bulb of which is about half-way down the inside of the bath. The air-bath may be employed not only for evaporating solutions in beakers to dryness, but also for drying at a particular temperature the residue left on evaporation.

The air-bath method is perhaps the safest of the methods of evaporating a solution. The temperature of the flame should be adjusted so that the liquid just does not boil. Under these conditions the water is removed at a fast rate, but the liquid does not bump. If a gentle current of filtered air is allowed to play over the surface of the solution, removal of the water may become quite rapid.

Comparatively high bath-temperatures are required for certain purposes. These can be obtained by using baths filled with graphite, or, better, with small rivets of brass or of aluminium bronze.

The Following Precautions should be observed during Evaporation :

(a) If effervescence occurs during evaporation, a tilted flask (Fig. 30, p. 32) may be used to avoid loss by spirting. Another plan is to use an evaporating-dish, and to cover it with a large inverted funnel as shown in Fig. 35. Vigorous boiling in an open vessel is necessarily accompanied by loss of substance.

(b) If the evaporation of a solution is conducted over a naked flame or over a sand-bath, the vessel should, if possible, be transferred to a water-bath towards the end of the process. This is advisable, because when a liquid has become thick and pasty by the separation of solid matter, it is apt to spirt considerably, even when it is heated comparatively slowly.

(c) Frequently the liquid creeps up the sides of the vessel during evaporation, particularly when it contains ammonium salts. The evaporation should then be carefully watched and the incrustation which forms near the edge of the vessel should be detached and pushed down by means of a glass rod. If the inner edge of the vessel is lightly greased, the ascent of the liquid will be prevented. If the liquid is heated from above (Fig. 52, p. 50), the ascent of the solution may also be prevented. In this case the vessel must be of metal or of some other material which conducts heat freely.

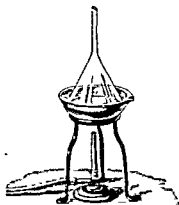


FIG. 35. PROTECTED EVAPORATION.

### Filtration and Washing of Precipitates

It is usual to determine the percentage of an element in a substance by dissolving the substance in some suitable solvent and by adding some suitable reagent which will combine with the element alone, to give an insoluble precipitate. By using a reagent in the correct quantity and by applying it under the correct conditions, it is possible to convert all the element into some insoluble compound. Instructions for the precipitation of certain of the elements will be given in Part II. When a precipitate has been obtained, the next step is to remove the liquid from it by filtration. This is usually done by passing the liquid through a suitable filter-paper, or porous plate. The papers which are commonly used are 9 or 11 cm. in diameter.

then thoroughly washed, in order to remove mineral matter. An 11-cm. filter

Choose a filter-funnel which is symmetrical and which has a stem some 8 to 10 cm. in length with an internal diameter of about 0.5 cm. The

cross-section of the end of the stem should be ground to angle of  $45^\circ$ . Fold the filter-paper firmly across the centre and then double the paper again, but this time making the fold with only a slight pressure. Open the paper at the larger division and fit it to the dry funnel. If the fit proves poor, tear up the paper and fold another to a slightly different size. It is important to choose a paper rather smaller than the funnel; a centimetre of glass should be exposed around the top edge, as it is then easier to wash the precipitate efficiently.

Now fill up the paper with hot, distilled water. Close the end of the stem with the finger and raise the paper slightly. See that the stem and the lower part of the funnel are completely full of water, and fit the paper to the glass as tightly as possible. Remove the finger from the stem and allow the water to flow away, meanwhile pressing the top of the paper, especially near the folds, to the glass. The water should pass rapidly through the paper and the flow should stop suddenly, leaving the stem



FIG. 36. FILTRATION.

full. No air should leak between the paper and the glass to collect in a bubble at the top of the stem. If the stem remains full of water, filtration is carried out under slightly reduced pressure and is thereby speeded up. Time spent on correctly folding a paper is never wasted.

A pleated filter-paper should never be used in quantitative work. Filtration through such a paper is little, if any, faster than through one folded as described above, while it is much more difficult to wash a precipitate collected in the pleats.

Filtration is usually combined with decantation in the following manner: The precipitate is allowed to settle; most of the clear fluid is then decanted off through the filter-paper without disturbing the precipitate (Fig. 36). After the liquid has been decanted through the filter, a fresh quantity of distilled water, or other washing liquid, is poured upon the precipitate, and the contents of the beaker are stirred or boiled. The precipitate is then allowed to subside, and the clear washing liquid is decanted off through the same filter. If, when the beaker is standing on the bench, it is supported by wooden blocks or other suitable supports

at 60° from the vertical, the precipitate will collect in the "corner" of the beaker. It will then be little disturbed when the beaker is again lifted, and therefore most of the liquid can be passed through the paper before any precipitate arrives to slow up the speed of filtration. These operations are repeated several times with fresh portions of distilled water. Finally the precipitate is transferred to the filter-paper by means of a fine stream of water from the wash-bottle. When handling a gelatinous precipitate it is particularly important to prevent the passage of small quantities of the precipitate to the paper during the early stages of decantation.

If the precipitate is reluctant to leave the beaker, the latter may be inclined over the funnel at an angle of 45°. A glass rod should be so held over the mouth of the beaker that any liquid runs along it into the funnel. A fast jet of water is then directed not *at*, but *above*, the precipitate. The greater part of even a heavy precipitate can be transferred by this method.

Sometimes the precipitate sticks to the glass. In this case it is often best to redissolve it in the least possible quantity of some suitable solvent and to reprecipitate it, using only a "corner" of the beaker. When this plan is not feasible, a "policeman" can be used. A "policeman" is a glass rod tipped with about an inch of smooth rubber tubing. The end of the rubber should be closed by a cap to prevent the solid working up between the tube and the rod.

The precipitate must then be washed. When possible use hot water and use only small quantities at a time, allowing the liquid to drain away completely after each addition. The jet of water should be directed at the top of the paper and the funnel should be rotated by hand when the jet is playing. "If you wash the top of the paper, the precipitate will look after itself." A simple calculation will show that it is much more efficient to wash four times, quarter-filling the funnel each time, than to wash *once* by completely filling the funnel.

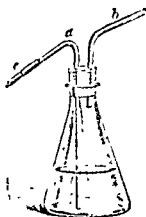


FIG. 37. WASH-BOTTLE.

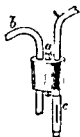


FIG. 38. VALVE FOR WASH-BOTTLE.

A Convenient Wash-bottle is shown in Fig. 37. It consists of a 500-ml. conical flask fitted with a rubber bung and glass tubes. The jet (c) is movable, since it is attached by rubber tubing to the tube (a). This enables the stream of liquid to be projected in any direction.

When Boiling Water, or a Liquid which gives off Vapour or Gas, is in the wash-

used to prevent the gas or (a) which terminates just above and just through the centre hole. The other holes carry the the ordinary bottle. The lower end of the blow valve by slipping over it a piece of rubber tube which has a slit cut in it as is shown at (c). The end of the rubber tube is closed by a piece of glass rod.

While the wash-bottle is being used the tube (a) is closed by the finger, and air is blown in through the valve (c). The valve (c) prevents the air from returning through the blow-tube, and no vapour or gas can therefore reach the mouth. As soon as the washing is finished, the finger is removed from (a) and the stream of liquid is thus stopped at once.

### Accelerated Filtration

**Acceleration by Lengthened Funnel.** One of the simplest means of increasing the rate of filtration is to attach to the funnel an ordinary glass tube, bent as is shown in Fig. 39. As soon as the filtrate has filled the tube, the weight of the column of liquid tends to draw the solution through the filter, and the rate of filtration is accordingly increased. In order to make the best use of this device it is essential to fit the paper so tightly to the funnel that there is no air leak. The point of the end of the funnel stem should be in contact with the side of the beaker; this avoids splashing by drops, and assists filtration by capillary action.

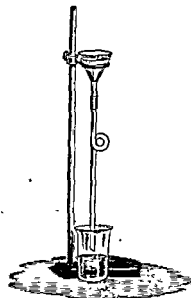


FIG. 39. ACCELERATED FILTRATION.

Another simple method is to attach to the funnel a straight piece of thick glass tube about 2 feet in length and only 1 mm. in bore. The liquid passes down the tube in a nearly unbroken column, the weight of which tends to draw the liquid through the paper.

**Acceleration by Filter Pump.** The most rapid filtration, however, is secured by reducing the pressure beneath the funnel by means of a pump. The full atmospheric pressure, which is still exerted on the surface of the liquid in the filter, forces the liquid through the filter.

The pressure thus brought to bear on the filter may be greater than ordinary paper in the wet condition can support. It becomes necessary, therefore, either to use specially prepared, toughened filter-paper, or to support the ordinary paper in a suitable way. Another means of obtaining a sufficiently resistant medium is to produce a filter from fine asbestos fibre in the manner described on p. 43; or the liquid may be filtered through a porous crucible or porous glass plate.

If filter-paper is used, it is fitted as follows: A funnel is selected, the sides of which form an angle of 60°. A muslin, platinum or porcelain cone (p. 42) is placed in the funnel; and then a dry filter-paper, folded in the ordinary manner, is inserted. The paper is pressed with the finger

until the supporting muslin or platinum and the paper fit the sides of the funnel closely. Then, being still held in position, the filter is wetted by pouring in a little distilled water. The overlapping edges of the filter-paper are next pressed down by the finger, and any air bubbles between the funnel and the paper are carefully removed. The funnel is then fitted by means of a perforated rubber stopper into the neck of a clean, strong, conical filtering-flask, of about 750 ml. capacity. The flask is connected up through a safety bottle with a suitable water-pump by means of the side-tube in its neck (Fig. 40).

Before filtration proper is started, it is well to fill the filter with distilled water and to start the pump. If any air is seen to be sucked down between

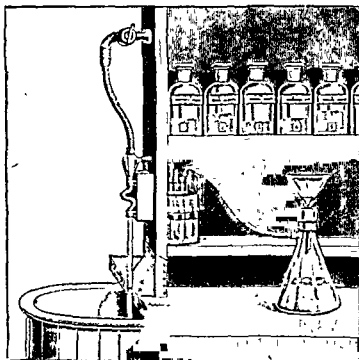


FIG. 40. ACCELERATED FILTRATION.

the filter and the funnel, this may be stopped by gently pressing the moistened edges of the paper against the glass.

The pressure should be reduced gradually, because the particles of certain precipitates are apt at first to pass through the pores of the paper. If the difference in pressure between the two sides of the paper is allowed to become high, the pores may be clogged by the precipitate being drawn into them. In consequence the rate of flow of the liquid decreases and the filter-pump may be a hindrance instead of a help. The optimum difference in pressure rarely exceeds one-tenth of an atmosphere.

During filtration and washing, liquid should be constantly poured into the filter so that it is never quite empty, otherwise fissures are apt to form in the mass of the precipitate. If this should occur, efficient washing becomes impossible, because the water passes through the fissures instead of through the whole of the precipitate.

The washing of gelatinous precipitates is very much shortened by the above procedure; moreover, if air is drawn through the precipitate for a

few minutes after the washing water has run through, the time required for drying the precipitate in the steam-oven is considerably reduced.

**The Water-Aspirator.** A convenient form of water-aspirator or filter-pump is that invented by Geissler (Fig. 41). Another form is shown in Fig. 40. The pump may be att

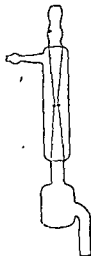


FIG. 41.  
WATER-PUMP.

copper wire.

This aspirator has three tubes fused into the chamber in the upper part. The upper vertical tube conveys the water, which passes through the contracted end of this tube into the opening immediately below it. During its free passage, after leaving the jet, the water draws air from the chamber and carries it

of its air.

The side-tube of the filter-pump is connected with a tube which passes to the bottom of a small two-necked bottle (Fig. 40). The other tube of this bottle passes just through the bung in the second neck, and is connected by rubber tubing with the side-tube of the filtering-flask. This two-necked bottle serves to lessen the chance that tap water may find its way back into the filter-bottle and mix with the filtrate. If, through some error, the water is turned off before the bottle is disconnected, the small volume of water in the pump will be sucked back and retained by the safety bottle. Needless to

say, the water supply should never be turned off without first disconnecting the filter-flask.

instead of by water.

**Special Filter-Paper, and Supports for the Filter,** when the filter-pump is employed, are described below.

(a) *Thin Toughened Filter-Papers* which will satisfactorily withstand a pressure of one atmosphere can now be obtained.

(b) *Toughened Paper, or Muslin Support.* If ordinary untoughened filter-

position over this support.

apex of the untoughened filter may also

To prepare this, a by 3 cm. broad, is pierced a little below its middle point by a pin (Fig. 42). A cut is made from the middle of the longer edge to this hole. The corners are then removed by cutting with scissors round the segment of an inscribed circle, whose



FIG. 42.  
PLATINUM SUPPORT.

to fit the funnel.

(d) *A Perforated Porcelain Cone support* may be used with either a paper filter or with an asbestos filter prepared by the Gooch method explained below.

**The Gooch Method of Filtration** through an asbestos filter is convenient and fast. The filter is made either in a crucible or in a porcelain cone. If a suitable crucible is used, the precipitate can be filtered, washed, dried, and ignited in the crucible itself.

Choose a crucible, some 4 cm. in height, with a capacity of 25 ml. and perforations 0.8 mm. in diameter. The general tendency is to use too small a crucible with holes which are much too small. Take a piece of rubber tubing about 1 inch in length, and of such a diameter that the bottom of the crucible, but not the top, can slide into it fairly easily. Select a funnel, preferably of the thistle type, of rather greater diameter at the top than the diameter of the bottom of the crucible. Fit up the apparatus as shown in Fig. 43.

Alternatively a slightly wider rubber tube can be used. The crucible is then pushed into the rubber until the bottom is well through. The crucible with its outer coating of rubber is now pushed into the thistle funnel. The fit should be quite tight. Finally, that part of the rubber tube which projects may be bent outwards over the outer wall of the funnel. The apparatus is then fitted to an ordinary filter-bottle or filter-flask. When the filtered liquid is to be examined, it is important that the stem of the funnel is long enough to reach below the side-tube of the filter-

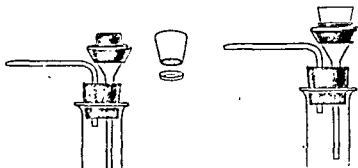


FIG. 43. GOOCH CRUCIBLE AND FITTINGS.

bottle so that any risk of the liquid being sucked out of the bottle is avoided. The crucible, especially if the liquid has oxidising properties, must be so arranged that the filtrate does not come into contact with the rubber during its passage to the bottle.

*Asbestos* for use in the crucible must be selected and prepared with care if the Gooch is to work rapidly and efficiently. Amphibole asbestos gives the best results, provided it is long-fibred. The dry asbestos is finely shredded by hand, the fibres are cut to lengths of about 0.5 cm., and then shaken on a 30-mesh sieve to get rid of dust. They are then boiled for half an hour with 20 per cent. HCl, filtered and washed in a Buchner funnel (Fig. 59) until free from chlorides, and shaken up with water in a large measuring-cylinder. When the suspension has been quiet for a short time, say a minute, in order to allow the coarser particles of asbestos to settle, the top liquor is poured off into some convenient vessel. The asbestos is then left to settle out completely, the top layer of water is poured off, and the residual mush of fibres and water transferred to a bottle. The contents of the bottle must be shaken before use, and water may be added from time to time.

*Making a Gooch.* The crucible is half-filled with the suspension of asbestos and water, and the water is allowed to drain away slowly with the pump running very gently. Then pump is then turned on full and the asbestos is pressed firmly down into the holes. If the end of a thick



glass rod is fused in the flame and flattened out by gently pressing the rod vertically downwards on an asbestos surface, a useful instrument for preparing a thin compact asbestos layer is obtained; this part of the process is largely a matter of experience. The asbestos is washed as follows: Turn the pump on gently and place the end of the glass rod on the centre of the pad. Then pour the washing liquid gently down the rod, raising the latter when there is a protective layer of liquid over the asbestos. When the Gooch is used for the collection of a precipitate the same procedure is adopted; the liquid must never be poured down the sides of the crucible in case it displaces the pad. The crucible is washed and dried initially in exactly the same way as it will be washed and dried when it contains the precipitate.

It is important to remember that the difference in pressure between the inside and the outside of the crucible during filtration must never be very great; a high pressure difference will jam the particles of the precipitate into the asbestos, and filtration will be slow.

*Porous Alundum Crucibles* can sometimes be used in place of Gooch crucibles. They consist chiefly of alumina, which is held together by a very small proportion of binding material, and are made in different grades of fineness. The coarse grade is useful for certain crystalline precipitates, the medium for ordinary work and the fine for precipitates of small particle size, such as barium sulphate and calcium oxalate. It is convenient to have a number of these crucibles, each of about 25 ml. capacity, in each grade.

They have proved excellent in use, and are manipulated in exactly the same way as a Gooch crucible is manipulated, except that, of course, no asbestos pad is required. They suffer from three disadvantages. As the whole material of the crucible is porous, soluble salts find their way into the sides, and it is rather difficult to wash the upper part of the crucible completely free from these salts. Further a very small quantity of alundum may be rubbed off the outside of a new crucible during the course of an experiment. More important, alumina is a hygroscopic material and therefore particular attention must be paid to the drying and weighing of alundum crucibles. For accurate work they must be weighed in stoppered weighing-bottles.

If the precipitate is removed either by shaking it out or by the use of some suitable solvent when an absolutely clean crucible is required, the crucible can be used again and again. The most efficient way of cleaning a crucible is by reverse washing. The apparatus (Fig. 44) consists of a wide-mouthed filter-bottle fitted with a large rubber bung. There is a hole in this bung, and the stopper also carries a short glass chimney. The crucible is inverted over the hole and it is surrounded above and below by the solvent liquid, which is pulled slowly through the crucible by the water-pump.

*Sintered Glass Crucibles* are also of great value. They are crucibles of blown glass, but a plate of sintered glass is fused into the bottom. This sintered plate is made by heating glass powder to a suitable

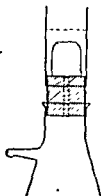


FIG. 44. APPARATUS FOR CLEANING SPECIAL CRUCIBLES.

temperature ; its porosity depends on the original grain size of the powder and, as this size can be controlled, crucibles suitable for different types of work can therefore be obtained. The crucibles are very clean and can filter liquids very rapidly, but it is inadvisable to use them for drying precipitates at high temperatures because the plate is apt to work loose from the crucible walls. Apart from this, like alundum crucibles, they can be used repeatedly.

The introduction of these three types of crucible has made gravimetric analysis a much easier and speedier process, so much so that the advantages of the use of filter-paper in complicated technical analyses are often apt to be overlooked in college laboratories, and not enough opportunity is there given to acquire the skill necessary to manipulate a precipitate and paper successfully.

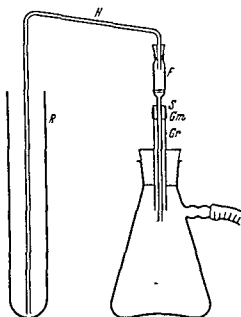


FIG. 45. SUCTION APPARATUS FOR MICRO-FILTRATION. (Half actual size.)

*R.* Wide test-tube. *H.* Syphon. *F.* Filter tube. *S.* Rubber stopper.  
*Gm.* Rubber collar. *Gr.* Adjustable glass tube.

Micro-Filtration is conveniently carried out in the apparatus shown in Fig. 45. The solution to be filtered is contained in the test-tube (*R*), and it is drawn over into the filter by suction applied at the side-arm of the flask, at the rate of about 2 drops per second. The filter (*F*) consists of a tube with a constricted neck, which fits inside a glass sleeve (*Gr*) held in the rubber bung of the suction flask. The actual filtering medium is a small plug of asbestos or sintered glass, in the space just above the constriction. The use of a policeman to collect the last traces of fine precipitate is avoided by adding a few drops of alcohol to the test-tube, after as much as possible of the filtrate has been transferred to *F* by the wash liquors ; these act as an aggregating agent. The apparatus is suitable for the determination of bromides and sulphates by precipitation with silver nitrate and barium sulphate, respectively.

## Drying and Ignition of Precipitates

After the precipitate has been collected, it must be dried. If a crucible has been used, it is frequently unnecessary to ignite the precipitate, so that here the drying is the final operation before cooling in a desiccator for weighing. The crucible is covered with a disc of filter-paper to exclude dust, placed on a watch-glass or clean plate and dried in an oven at some suitable temperature to constant weight. A steam-chamber is sometimes used, but more frequently it is best to dry in an air-oven at  $105^{\circ}$  to  $110^{\circ}$  C. If the precipitate is to be ignited, it is sometimes advisable to dry it as described above, but more often it is possible to proceed directly as follows: A nickel crucible considerably larger than the filter-crucible is chosen. The bottom is covered with a thin layer of ignited asbestos and the asbestos by a platinum or porcelain plate on which the filter-crucible is placed. The large nickel crucible is covered partly or wholly with its lid, and is heated by one of the methods to be described later. If the precipitate is wet it is advisable to raise the temperature slowly.

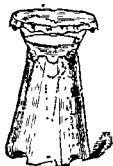


FIG. 46.  
FILTER-DRYER.

If a filter-paper has been used, the precipitate is dried by covering the funnel with a piece of paper to exclude dust, and placing the funnel in a steam-oven. Steam-ovens are nearly always provided with shelves perforated with holes to receive the stems of the funnels, but a truncated iron cone (Fig. 46) or any other suitable arrangement which allows the hot air to circulate freely round the funnel and so to dry the precipitate, may be used. It is nearly always profitable to allow the precipitate to become thoroughly dry before making any attempt to burn the paper.

The paper must now be burnt, and the weight of the ash (see p. 37), if appreciable, must be subtracted from the total weight of the ignited precipitate and filter-ash. Sometimes the ignition of the precipitate and the incineration of the filter may be combined in one operation, but the two processes must be conducted separately if the composition of the precipitate is affected by the burning paper.

The Weight of the Filter-ash is usually less than a milligram, and may be negligible. This weight is generally printed on the packet of papers, but if necessary it may be found as follows:

Six of the cut filter-papers are selected from different parts of the packet, or six circular filter-papers are cut out of precisely the same size from different sheets of the paper. These are carefully folded and burnt, one by one, in a weighed platinum crucible until the ash is white. The crucible and the ash are then weighed. The total weight of the ash, divided by six, will give the average weight of the ash from one filter-paper.

The Vessels used for the Ignition of precipitates which have been collected in filter-papers are crucibles or capsules made of platinum, silver, nickel, porcelain, or fused silica.

A Platinum Vessel should be used in quantitative work whenever considerations of suitability and cost permit.

Platinum crucibles can be more rapidly and uniformly heated than those made of porcelain, and they are not so fragile; they resist the action of a coal-gas flame better than does nickel, and they are practically

infusible. A crucible 3 cm. in height and 3 cm. in diameter will be found convenient for most purposes. A small open platinum dish or capsule will often be found more convenient than a platinum crucible for ignitions. The dish may be about 5 cm. in diameter, and have an extreme depth of about 2 cm.

Platinum should *never* be employed under the following conditions :

(i.) In the presence of fused caustic alkali. Fused alkali carbonate is permissible if care is exercised. Fused alkaline nitrates, peroxides, nitrites, and cyanides also attack platinum.

(ii.) In the presence of compounds of such easily-reducible metals as As, Sb, Bi, Zn, Pb, or Sn.

(iii.) In the presence of Si, S, Se, Te, or P. Sulphides should never be ignited in platinum vessels, and phosphates only under circumstances which make impossible the production of free phosphorus or a phosphide.

(iv.) It should never be heated in a sooty or luminous flame or in the inner cone of a Bunsen flame. This will eventually produce a carbide of platinum, which, though it may resemble the original metal in appearance, is much more brittle.

(v.) In the presence of a mixture of nitric and hydrochloric acids (though each separately is permissible), or of solutions containing chlorine. Obviously this injunction also applies to solutions containing hydrochloric acid and a nitrate, or nitric acid and a chloride. Long contact with a solution containing ferric chloride is also injurious.

(vi.) Hot platinum should never be touched with brass tongs, or zinc from the tongs will alloy with the platinum. Clean iron tongs, or, preferably, tongs tipped with platinum or gold should be used.

(vii.) During prolonged heating, platinum should never come into contact with any other metal whatsoever. Thus the use of bare Nichrome supports is precluded. Platinum ware should be supported on glass or porcelain rings (see p. 35), when being heated on a water-bath.

**The Cleaning** of platinum vessels should be carried out with care. The use of a knife, file, or even of an untipped glass rod should be absolutely forbidden, though burnishing with fine sea-sand whose grains are rounded and so small that they will pass a 100-mesh sieve, or with very fine carborundum powder, is permissible and even desirable. The solvent to be used for cleaning platinum vessels depends, of course, on the nature of the impurities present. Concentrated hydrochloric acid will remove many metallic oxides, gentle fusion with potassium bisulphate will remove many acid-insoluble oxides, and a sodium carbonate or borax fusion will remove silicates. Organic residues can often be attacked by a mixture of sulphuric and chromic acids, though care must be taken to see that this mixture is absolutely free from chlorides. Potassium bisulphate, despite the fact that it has a definite, though slight, solvent action on platinum, is perhaps the most generally useful of these reagents. Sodium amalgam is useful for cleaning platinum, especially if base metals are present in the surface. The amalgam is wiped carefully over the surface with a soft cloth; the surface is then moistened with water and again wiped to remove the amalgam of Hg with base metals, and finally heated to redness to drive off the residual Hg. Platinum ware not in use should always be kept in a boxwood former having the exact shape of the vessel.

**Silver or Nickel** vessels are available for fusions with caustic alkali, but as their weight generally changes on heating, they are not suitable for quantitative work. As the melting-point of silver is low ( $961^{\circ}\text{C}.$ ), silver vessels must not be heated strongly. They should be cleaned by burnishing with sea-sand.

**Porcelain Vessels** are much less costly than platinum vessels, and may be used for the same purpose; they are quickly attacked by fused caustic alkali and by fused lead oxide, and cannot be rapidly heated and cooled without risk of fracture.

**Fused Silica** vessels are not rapidly broken by rapid change of temperature. They may be used for acid substances, but not for fused or dissolved alkalis or even for strongly basic oxides such as  $\text{PbO}$  and  $\text{CaO}$ . They are practically infusible, and the loss of weight which they undergo by use and cleaning is less than that of platinum, while the weight for equal capacity is about the same. On the other hand, they lose in weight on prolonged heating owing to volatilisation of the silica. If their use under these conditions is unavoidable, the extent of this loss should be determined by weighing an empty dish before and after heating, for the same time, and at the same temperature, and used as a correction.

**Recrystallised Alumina** crucibles ( $\text{Al}_2\text{O}_3$ , over 99.0 per cent.; melting-point, above  $1,960^{\circ}\text{C}.$ ) are now obtainable. They are much cheaper than platinum and resist reducing gases, many fused salts, metals, concentrated alkaline solutions and boiling sulphuric acid. They are, however, less resistant to rapid heating or cooling than is silica.

**Prevention of Reduction or Oxidation during Ignition.** When a reducible precipitate is being heated, care must be taken that the flame does not come into contact with the interior of the crucible. This is best avoided by applying a small flame to the bottom of the slanted crucible, or by sitting it in a hole of the correct size cut in a piece of good asbestos sheet.

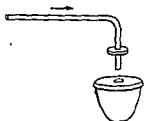


FIG. 47. ROSE CRUCIBLE.



FIG. 48. IGNITION IN GAS.

inverted bowl takes the place of the lid (Fig. 48).

The Crucible is usually Supported on a pipe-clay triangle or on a triangle made of stout platinum or Nichrome wires twisted together (Fig. 49). Triangles with coverings of fused silica may also be used. The pipe-clay

triangle should have a projecting edge in the middle of each side (Fig. 49). These strengthen those parts of the triangle which are most subject to wear and breakage, and also allow of more uniform heating, because the flame surrounds the crucible better.

The Temperature and Duration of the Ignition will vary with the nature of the precipitate.

In all cases the heat should be applied gradually. This is particularly necessary when the substance is imperfectly powdered, when it is not perfectly dry, or when it is in the form of a very light powder.

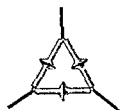


FIG. 49. PIPE-CLAY TRIANGLE.

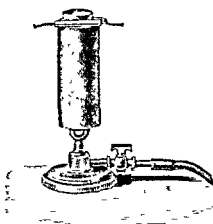


FIG. 50. IGNITION OVER THE WALLACE-ARGAND BURNER.

The Ordinary Method of Ignition by means of a Bunsen Burner is shown in Figs. 51, 52. The crucible rests on a pipe-clay triangle on the ring of a tripod stand or of a retort stand. A retort-stand (Fig. 52) is generally to



FIG. 51. IGNITION IN PORCELAIN CRUCIBLE.

be preferred as a support, because the height of the crucible above the flame can be suitably adjusted.

When Loss of Liquid by Spiriting might occur, the Substance is Heated from Above. The crucible containing the substance is inclined as is shown

in Fig. 52. A small flame is placed under the upper edge, and the substance is heated partly by heat radiated from the lid, and partly by the conduction of heat down the side of the crucible. The ignition is finished by placing the flame immediately below the bottom of the crucible.

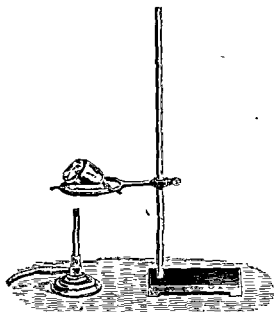


FIG. 52. IGNITION, AVOIDING LOSS OF SPIRITING.

Ignition at Higher Temperatures is secured by using the foot blowpipe, but for most purpose the Fletcher safety bunsen or the Méker burner will amply suffice. These burners are specially designed to yield a "solid" high-temperature flame, which will melt copper.

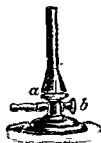


FIG. 53.  
TECLU BURNER.

Another form of high-temperature burner is the Teclu burner (Fig. 53), in which the air supply enters the conical portion of the burner and is regulated by rotating the disc (a), while the screw (b) regulates the supply of gas. When a high temperature is required, the full supply of gas is turned on, and the disc is then rotated until a roaring flame is produced.

The ignition of precipitates at high temperatures, however, is most conveniently carried out in a muffle furnace heated either by electricity or by gas, and so designed that a current of clean air can be drawn at will over the crucible. The temperature should be measured by a suitable pyrometer.

### Ignition of the Precipitate and Incineration of the Filter in one Process

This method is used when the combustion of the filter-paper can exert no harmful action upon the precipitate. The filter and precipitate are first thoroughly dried in the steam-oven. The filter-paper, still containing the precipitate, is then folded together and the free edge of the paper is turned down, so as to enclose the precipitate in as small a space as possible. The paper is now placed in the crucible, which is

nearly covered with the lid, a small space only being left for the escape of any gas.

The heat must be applied slowly at first, but as soon as the flame due to the burning of the combustible gases is no longer seen, the lid may be removed, and the heat may be increased as required. Slow heating is necessary, because the carbon of filter-paper may change to graphite if it is heated rapidly to a high temperature. As graphite is much more difficult to burn than is amorphous carbon, time may be lost instead of gained by rapid heating. After the filter-paper has been converted into ash, and the black carbon from the paper has been completely burnt, the crucible is allowed to cool. As soon as it has cooled below redness, it is removed by means of a pair of *clean* crucible tongs to a desiccator. The crucible lid is then ignited, if necessary, until it is clean, and is placed upon the crucible. The crucible is weighed with its contents as soon as it is cold. It will usually require about twenty minutes to cool. *The crucible should be heated and cooled a second time and, if necessary, a third and fourth time, until its weight is constant*, and it is a good plan to standardise this procedure, so that the crucible cools for the same time both when empty and finally; if this is not done errors may arise with crucibles which cool only slowly (e.g., heavy porcelain crucibles in a warm laboratory).

If the Filter-Paper is Difficult to Burn and black particles of carbon persist, the crucible should be allowed to cool. Then, provided the nature of the precipitate allows, the cold ash is moistened with a drop of a saturated solution of ammonium nitrate. Next, the water is slowly removed and the precipitate is again ignited. The paper will seldom be difficult to burn if the initial heating has been carried out slowly.

**Ignition of the Undried Precipitate.** Some precipitates may be ignited without previous drying in the steam-oven. In this case great care must be taken to avoid spattering. If a porcelain or silica crucible is being used it is probably best to heat it first on an asbestos mat or thin iron plate until the paper has thoroughly charred. The crucible is then transferred to a triangle and the ignition completed in the ordinary way. If a platinum crucible is available, the paper can be dried by heating from above (Fig. 52), and the flame should not be moved to the bottom of the crucible until it is certain that all the paper is thoroughly dry.

### Ignition of the Precipitate, and Separate Incineration of the Filter

This process is used when the burning filter-paper might partially reduce the precipitate, and also when it is desirable to keep the precipitate apart from the filter-ash. Two methods are described below.

**First Method. The Filter is Burnt in a Platinum-wire Coil, and the Ash and the Precipitate are Ignited together in the Crucible.** The dry precipitate and filter are taken from the funnel, and the precipitate is carefully shaken out of the filter into the crucible or capsule.

The crucible should meanwhile be placed on a piece of glazed paper (Fig. 54), which catches any particles of precipitate which may fall outside the crucible. For dark precipitates, white paper may be used; for light coloured precipitates, use dark paper. So far as possible, particles of the precipitate which remain adhering to the filter-paper should be detached



by gently rubbing the sides of the paper together, and then transferred to the crucible. If a spatula is used for any of these operations, it should

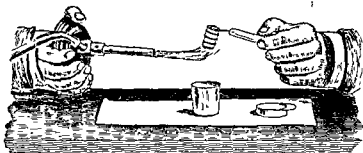
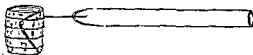


FIG. 54. INCINERATION OF THE FILTER.

finally be wiped clean of any precipitate on a piece of the filter-paper, which is then also added to the crucible.

The filter-paper is now folded as is shown in Fig. 55, and it is then rolled up (Fig. 56). Next it is bound by a piece of platinum wire, which is coiled round it in a spiral form. Some fairly stout platinum wire about 6 inches in length, one end of which has been fused into a piece of glass rod, will be found suitable.

The filter-paper is then kindled by the flame of a horizontally-held Bunsen burner, and is kept glowing by occasionally introducing it into



FIGS. 55, 56. PREPARING FILTER FOR INCINERATION.

the flame until the carbon is burnt away. A slight tap of the wire on the edge of the crucible will cause the ash to fall into the crucible. If the wire has been coiled into a conical spiral, the folded filter may be dropped into it, and the ash may be easily turned out after the ignition by simply inverting the spiral. Any particles of the precipitate or of the filter-ash which may have fallen upon the sheet of glazed paper are then carefully transferred to the crucible by means of a small camel's-hair brush, and the crucible and its contents are ignited, allowed to cool in the desiccator, and weighed.

The use of a spirit flame at this stage is recommended. If a Bunsen burner is used as is shown in Figs. 54 and 57, great care must be taken to see that it is quite clean, or pieces of scale from the tube of the burner may fall into the precipitate. To light the paper with a match is to run the risk of the burnt head falling where it is not wanted.

If the Precipitate contains a Metal, which may be reduced by the burning paper and then may alloy with the platinum wire, great care must be taken to fold the filter so as to enclose the adherent precipitate in the *middle* of the paper coil. However, in this case it is preferable to use the second method of incineration.

If the Substance can be Altered in Composition by Contact with the Burning Paper, it is usually necessary to treat the filter-ash with a suitable reagent, in order to restore that part of the substance which has been ignited on the paper

to its original composition. In this case the ash is allowed to fall upon a separate part of the bottom of the crucible or capsule: the ash can then be treated apart from the main part of the precipitate. An alternative method is described below.

**Second Method. The Filter is Burnt in the Crucible and the Precipitate is then Added and Ignited.** This method gives satisfactory results with careful manipulation, but it will be seen that there is a greater risk of loss of precipitate than in the preceding method. The procedure is as follows:

The precipitate is carefully transferred to a watch-glass or to a piece of glazed paper, and is covered with an inverted funnel (Fig. 57).

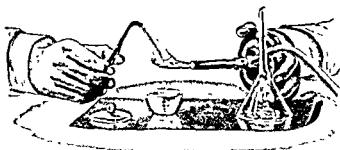


FIG. 57. INCINERATION OF THE FILTER.

The paper is then folded up and is incinerated by heating it in a crucible. Or the filter may be held by clean crucible tongs in the flame, but over the crucible, until most of the carbon has burnt off; the residue is allowed to drop into the crucible, and the ignition is finished over the Bunsen flame. The precipitate is then placed in the crucible, a small camel's-hair brush being used to sweep the last particles from the glazed surface. Finally, the crucible and its contents are ignited at the appropriate temperature.

### Preparation of Pure Substances

The use of pure substances for practice and as standards in quantitative analysis is sometimes indispensable. Some general methods for purifying substances are therefore described in the following paragraphs. Pure chemicals can now, however, usually be bought under a guarantee; the products specially prepared for analytical work (as indicated on the label on the bottle) should be chosen, as they contain less than the minimum quantity of any particular impurity which is likely to affect any determination in which they are used.

**The Process of Crystallisation** is used for the preparation of pure substances and of double salts.

The purity of a soluble and crystalline chemical compound can usually be increased by dissolving it in a suitable medium and repeatedly crystallising it, since by this treatment the impurities which were present in the original substance are left behind in the mother-liquor. Many commercial salts may be purified by crystallising them once or twice from their solution in water.

Double salts can usually be made by dissolving their component salts in

by gently rubbing the sides of the paper together, and then transferred to the crucible. If a spatula is used for any of these operations, it should

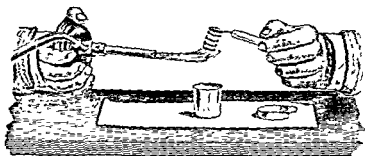


FIG. 54. INCINERATION OF THE FILTER.

finally be wiped clean of any precipitate on a piece of the filter-paper, which is then also added to the crucible.

The filter-paper is now folded as is shown in Fig. 55, and it is then rolled up (Fig. 56). Next it is bound by a piece of platinum wire, which is coiled round it in a spiral form. Some fairly stout platinum wire about 6 inches in length, one end of which has been fused into a piece of glass rod, will be found suitable.

The filter-paper is then kindled by the flame of a horizontally-held Bunsen burner, and is kept glowing by occasionally introducing it into



FIGS. 55, 56. PREPARING FILTER FOR INCINERATION.

the flame until the carbon is burnt away. A slight tap of the wire on the edge of the crucible will cause the ash to fall into the crucible. If the wire has been coiled into a conical spiral, the folded filter may be dropped into it, and the ash may be easily turned out after the ignition by simply inverting the spiral. Any particles of the precipitate or of the filter-ash which may have fallen upon the sheet of glazed paper are then carefully transferred to the crucible by means of a small camel's-hair brush, and the crucible and its contents are ignited, allowed to cool in the desiccator, and weighed.

The use of a spirit flame at this stage is recommended. If a Bunsen burner is used as is shown in Figs. 54 and 57, great care must be taken to see that it is quite clean, or pieces of scale from the tube of the burner may fall into the precipitate. To light the paper with a match is to run the risk of the burnt head falling where it is not wanted.

If the Precipitate contains a Metal, which may be reduced by the burning paper and then may alloy with the platinum wire, great care must be taken to fold the filter so as to enclose the adherent precipitate in the middle of the paper coil. However, in this case it is preferable to use the second method of incineration.

If the Substance can be Altered in Composition by Contact with the Burning Paper, it is usually necessary to treat the filter-ash with a suitable reagent, in order to restore that part of the substance which has been ignited on the paper

to its original composition. In this case the ash is allowed to fall upon a separate part of the bottom of the crucible or capsule: the ash can then be treated apart from the main part of the precipitate. An alternative method is described below.

**Second Method. The Filter is Burnt in the Crucible and the Precipitate is then Added and Ignited.** This method gives satisfactory results with careful manipulation, but it will be seen that there is a greater risk of loss of precipitate than in the preceding method. The procedure is as follows:

The precipitate is carefully transferred to a watch-glass or to a piece of glazed paper, and is covered with an inverted funnel (Fig. 57).

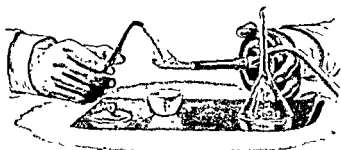


FIG. 57. INCINERATION OF THE FILTER.

The paper is then folded up and is incinerated by heating it in a crucible. Or the filter may be held by clean crucible tongs in the flame, but over the crucible, until most of the carbon has burnt off; the residue is allowed to drop into the crucible, and the ignition is finished over the Bunsen flame. The precipitate is then placed in the crucible, a small camel's-hair brush being used to sweep the last particles from the glazed surface. Finally, the crucible and its contents are ignited at the appropriate temperature.

### Preparation of Pure Substances

The use of pure substances for practice and as standards in quantitative analysis is sometimes indispensable. Some general methods for purifying substances are therefore described in the following paragraphs. Pure chemicals can now, however, usually be bought under a guarantee; the products specially prepared for analytical work (as indicated on the label on the bottle) should be chosen, as they contain less than the minimum quantity of any particular impurity which is likely to affect any determination in which they are used.

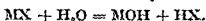
**The Process of Crystallisation** is used for the preparation of pure substances and of double salts.

The purity of a soluble and crystalline chemical compound can usually be increased by dissolving it in a suitable medium and repeatedly crystallising it, since by this treatment the impurities which were present in the original substance are left behind in the mother-liquor. Many commercial salts may be purified by crystallising them once or twice from their solution in water.

Double salts can usually be made by dissolving their component salts in

suitable proportions in as little hot water as possible, and crystallising the mixed solutions. It should be noted, however, that in the preparation of a double salt it is sometimes necessary to mix the component salts in proportions different from those in which they are present in the double salt.

**The Crystallisation of Salts.** The following is the usual procedure. A beaker, or flask, or a porcelain dish is used for the dissolution of the solid. A hot, saturated solution of the solid in water, or in some other suitable solvent, is made by stirring the finely-crushed solid with the hot liquid until the solid no longer dissolves. The hot clear solution is then decanted or filtered from the excess of solid into a crystallising dish.



The resulting hydroxide reacts with the excess of salt to form an insoluble basic salt. The solution then becomes cloudy. This may be prevented

by adding to the water a few drops of the acid corresponding with the acid radical which is present in the salt, *before* the salt is added. If any suspended matter is present, the solution must be filtered in a funnel surrounded by a hot-water jacket.



FIG. 58. HOT-WATER FILTER-JACKET.

The apparatus is shown in Fig. 58. It is a double-walled copper vessel in the shape of a truncated cone. In communication with the interspace of this is a hollow projection (a). The

apparatus is half-filled with water, and the water is heated to boiling by placing a Bunsen flame beneath the projection.

The clear hot solution is received in a thin glass vessel which is surrounded with cold water, and the solution is constantly stirred while it is cooling, to promote the formation of small crystals. Larger crystals may be obtained by allowing the solution to cool slowly, but these are liable to contain enclosed mother-liquor and to be less pure than small crystals. As soon as the crystals have ceased to form they are separated from the mother-liquor by means of a Buchner funnel (Fig. 59). These funnels are nearly always made of porcelain. In the centre of the funnel is a perforated plate which is covered with a circular filter-paper. For ordinary work a funnel, some 9 cm. in diameter, with a capacity of about 200 ml., is a convenient size. The funnel is fitted into a filter-flask, as shown in the figure.

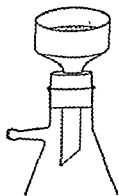


FIG. 59. BUCHNER FUNNEL.

To separate the crystals, first wet the paper with a small quantity of distilled water. See that the paper is tight up against the holes, and draw off excess of water by turning on the water-pump. Then empty the contents of the crystallising-dish into the funnel, draw off the liquor, and press the crystals down by pushing them with the flat top of a glass stopper. When they appear to be dry, wash them rapidly with successive small quantities

of cold water, finally again pressing them down with the glass stopper. Leave them to dry in the stream of air sucked in by the pump.

When the crystals appear to be dry they are broken up and transferred to an unglazed, porous plate. If they are left on this plate for 24 hours they will dry, especially if they are turned over with a glass rod. If a final drying is necessary, it may be carried out by pressing thin layers of the crystals between filter-paper. During crystallisation and collection, the crystals must be shielded from dust.

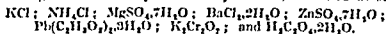
*The Practice of Drying* crystals in a desiccator, in a steam-oven, by washing with alcohol or even by drying on the hot-water radiators is strongly to be deprecated unless it is known definitely that the dry crystals do not change in composition during such treatment. Many substances contain water of crystallisation and easily lose all, or a portion, of it. For example,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  becomes  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  on heating in air to  $100^\circ \text{C}$ ., but is perfectly stable at room temperature. Any hydrate exerts a definite vapour-pressure of water at a definite temperature, the pressure increasing rapidly with an increase in temperature. If the crystals are placed in an atmosphere where the vapour-pressure of water is lower than that of the hydrate at that temperature, as in a desiccator or steam-oven, a change in chemical composition will take place.

Certain salts, such as  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , lose water on standing in the air of a laboratory; they effloresce. Others, such as  $\text{CaCl}_2$ , take up water from the air and deliquesce, because the vapour-pressures of their saturated solutions are less than the pressure of water vapour present in the air. Efflorescent and deliquescent substances are difficult to prepare and maintain in a pure state. Therefore they are unsuitable for use as standards in analytical work.

EXPERIMENT 11. Weigh out about 120 grm. of potassium alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , and dissolve in 100 ml. of boiling distilled water to  
Filter the solution  
tals and place them

EXPERIMENT 12. Weigh out about 100 grm. of copper sulphate crystals,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; dissolve the salt in 100 ml. of boiling distilled water, crystallise, dry the crystals, and place them in a bottle for subsequent use.

The following substances may also be crystallised, and used as standards:



**In the Formation and Crystallisation of Double Salts**, the method used varies with the properties of the substances.

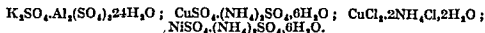
The usual method of preparing a double salt consists in weighing out the simple salts in the molecular proportions in which they are contained in the double salt. A hot, concentrated solution is then made of each salt separately; these two solutions are mixed together, and the liquid thus obtained is crystallised.

This method, however, cannot always be employed, since a solution of the component salts, prepared as is directed above, occasionally will deposit not only crystals of the double salt, but also of one of the component salts. This difficulty is overcome by using an excess of the other salt. It follows that if the once-crystallised double salt is required in an

absolutely pure state a certain proportion of the latter salt must also be added during the second crystallisation, or the product of this recrystallisation may be less pure than were the original crystals.

**EXPERIMENT 13.** Preparation of  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . Weigh out 87 grm. of pure  $\text{K}_2\text{SO}_4$  and 160 grm. of pure  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . It will be noticed that the weight of the  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is in excess of the molecular proportion. Dissolve these salts separately in boiling distilled water to which a few drops of dilute sulphuric acid have been added; mix the solutions, crystallise, and dry the crystals of the double salt.

The following double salts may also be prepared, using the molecular proportions of the component salts denoted by the formulæ of the double salts. The weighed salts are dissolved in the least possible quantity of boiling water, and are treated as described above.



**EXPERIMENT 14.** Preparation of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . Weigh out 70 grm. of pure crystallised  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and dissolve in 120 ml. of hot, distilled water.

Allow to stand for two hours and collect, drain, wash, and dry the crystals. As this double salt is very stable, it is permissible to hasten the drying process by carrying out the final washing with a little pure methylated spirit.

### Other Methods of Preparing Pure Substances

By Precipitation and subsequent Washing and Drying, many chemicals may be prepared in a pure state.

**EXPERIMENT 15.** Preparation of Pure  $\text{CaCO}_3$ . Dissolve 100 grm. of pure calcium chloride in 250 ml. of distilled water. Heat the solution to boiling, filter if necessary, and then add a concentrated solution of  $(\text{NH}_4)_2\text{CO}_3$ , so long as any precipitate is formed. Allow the precipitate to settle, and wash it by decantation. Now transfer the precipitate to a Buchner funnel; then wash it with hot water until the filtrate no longer gives any turbidity with  $\text{AgNO}_3$  solution, showing that all the dissolved chloride has been removed.

The precipitate is now completely dried in a steam-oven, detached from the filter-paper, and placed in a bottle for further use.

Pure  $\text{BaCO}_3$  and  $\text{SrCO}_3$  may be prepared in a similar way.

**EXPERIMENT 16.** Preparation of Pure  $\text{NaCl}$ . Dissolve 100 grm. of  $\text{NaCl}$  in 400 ml. of distilled water, and filter if necessary. Precipitate the  $\text{NaCl}$  by adding a concentrated solution of  $\text{HCl}$ ; or by passing into the solution a current of  $\text{HCl}$  gas, prepared by dropping concentrated sulphuric acid into a concentrated solution of hydrochloric acid and cleaned by bubbling the gas through a wash-bottle containing a little concentrated sulphuric acid, which also removes any spray. The delivery tube should have an inverted funnel attached to it by a piece of rubber tubing, and the mouth of the funnel should dip just below the surface of the sodium chloride solution. This precaution is necessary in order to prevent the salt solution from "sucking back" into the concentrated sulphuric acid.

The passage of the gas into the solution will precipitate the  $\text{NaCl}$  as small crystals. As soon as the precipitation ceases, the  $\text{NaCl}$  is washed twice by decantation with pure concentrated  $\text{HCl}$  and transferred to a Buchner funnel, washed once or twice with a small quantity of cold water and drained. If necessary the salt is then placed on a porous plate, and is finally freed from  $\text{HCl}$  and from water by heating it in a porcelain dish over a small Bunsen flame.

This pure dry  $\text{NaCl}$  is preserved for use in a stoppered bottle.

**EXPERIMENT 17.** Preparation of Pure Anhydrous Tartar Emetic. Dissolve 100 grm. of tartar emetic,  $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ , in the smallest possible quantity of water. Add to this solution about twice its volume of methylated spirit. Wash the salt thus precipitated with methylated spirit, and dry it at once in a steam-oven. The product will be anhydrous.

Sublimation is used occasionally to separate volatile from non-volatile substances. If a volatile substance is to be purified, sublimation may be carried out by placing the substance in a porcelain crucible, and inverting another crucible over it. When the lower crucible is gently heated, the substance will volatilise and the vapour will condense in the upper crucible, which must be replaced if it becomes hot. Another method consists in heating the substance in a porcelain dish, and condensing the vapour in a large inverted funnel covering the dish.

Unless the substance which is to be sublimed is known to be perfectly dry, it is best to allow the first portion of its vapour to escape, so as to carry off the moisture.

**EXPERIMENT 18.** Purification of Iodine. Partly fill a porcelain crucible with a finely-powdered and intimate mixture of three parts of iodine with one part of potassium iodide. Cover this with a second crucible, and heat the mixture gently. Remove the sublimed crystals from the upper crucible, and store them in a clean dry bottle.

The addition of potassium iodide to the iodine, followed by sublimation, removes chlorine and bromine from the iodine:  $Cl_2 + 2KI = 2KCl + I_2$ .

**EXPERIMENT 19.** Resublimation of Arsenious Oxide. Introduce into a small porcelain dish a thin layer of  $As_2O_3$ . Invert over this a clean glass funnel, and heat the dish gently in a fume-cupboard. Detach the sublimate from the funnel, and keep it in a bottle for future use.

### General Rules for Working

Many rules and precautions have already been given among the foregoing general directions for the carrying out of analytical processes. In the following statement these directions are summarised, and others are added which will be of great assistance to the student.

1. Before commencing work, see that all reagent bottles are full.
2. Keep the benches scrupulously clean and dry.
3. All apparatus should be kept perfectly clean. Methods of cleaning glassware are given on p. 107.
4. Before commencing the quantitative analysis of a substance of unknown composition, a careful qualitative analysis should invariably be made.
5. Before starting any unfamiliar analytical process, read carefully through the whole of the description given, and master its details.
6. Never place a substance directly on the scale-pan of the balance, but put it in a weighing-tube or other suitable vessel. Clean pieces of metal, however, may be weighed directly.
7. No substance which gives off corrosive gas or vapour should ever be weighed on a delicate balance, unless it is contained in a tightly-stoppered bottle.



8. When a weighing is finished, note down the weight at once in a notebook (not on any odd piece of paper), and check it. Take care that the weight is entered correctly, since one slip will ruin an analysis.

9. Never leave weights on the scale-pan after a weighing has been finished and the weights recorded; always close the balance-case as soon as a weighing is completed.

10. After a body has been heated, it should be allowed to cool in a desiccator before it is weighed, and it should be weighed as soon as it is cold; observe the precaution indicated on p. 51.

Crucibles should be heated shortly before they are used, then allowed to cool in a desiccator and weighed. These processes should be repeated each time a crucible is used. If it is known that the crucible does not lose weight when heated to the ignition temperature, it is sufficient to warm it only to about  $200^{\circ}\text{C}$ . during the preliminary drying. The temperature can be gauged by bringing the warm crucible near to the cheek. Very hot crucibles, loaded or unloaded, should be allowed to cool down in the air to just above  $100^{\circ}\text{C}$ . before being transferred to the desiccator, because they cool comparatively slowly when enclosed in a glass vessel.

11. All splashing while filtering and pouring off liquids must be avoided. A liquid may be poured from one vessel to another by pressing a wetted glass rod against the edge of the upper vessel, and leading the liquid along it to the inside surface of the lower one. If the outer edge of the upper vessel is thinly greased, the chances of loss of the liquid by dribbling down the outside will be substantially decreased.

12. The kind of crucible to be used in an analysis depends on the nature of the substance to be handled. The limitations are set out on pp. 46-49. For the use, cleaning and care of platinum, see p. 46.

13. A flame which is used for heating crucibles should be free from luminosity and strong colour. If the flame is luminous it will deposit soot on the vessels with which it is in contact. If it is coloured, it will probably deposit zinc or copper, or the oxides of these metals.

14. If an operation is unfinished when work ceases, the vessels containing the substances should be labelled before they are put away. *Never trust to memory in these matters.*

## PART II

# SIMPLE GRAVIMETRIC DETERMINATIONS

## SECTION IV

**Introductory Remarks.** In the following sections, the most important and typical processes are printed in ordinary type; those which are of less importance are printed in smaller type. The determinations of metals and of acid radicals are arranged, on the whole, as exercises of increasing difficulty, rather than in the order of the analytical groups. Many of the methods can be carried out on the micro-scale (see p. 251) in the apparatus described on p. 45, but applications of this kind should not be undertaken by the student until he is fully proficient in manipulating the larger quantities; in highly-accurate micro-work a blank determination should be carried out on the reagents used.

As most of the determinations are to be carried out on substances of known and definite composition, the accuracy of a student's result can be checked by calculation. When the substance is of unknown composition, two determinations should be made. It is usual to consider the percentage result obtained sufficiently accurate if it does not differ by more than 0.2 from the duplicate result or from the calculated theoretical result. For example, it is known that pure copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , contains 25.45 per cent. of copper; a determined value of from 25.25 to 25.65 per cent. would therefore ordinarily be accepted. This allowance of 0.2 per cent. is quite arbitrary, and must only be used as an approximate guide. It is obviously too generous when a substance contains only a small percentage of the element to be determined, and it may be too narrow when the substance contains a large percentage. The error inherent in the method should also be taken into account.

**Errors in Gravimetric Analysis.** It is generally assumed that the results of gravimetric analysis are extremely accurate, and there is a tendency to forget that this is so only when certain errors have been taken into account or when the work has been carried out in such a way (generally by doing a check determination on known materials in parallel with the assay) that these errors have been excluded.

As a source of error, consider solubility. Very few chemical compounds are truly insoluble in pure water, and fewer still are insoluble in a solution from which they have been precipitated. Silver chloride is generally regarded as a very insoluble compound, but 1 litre of water will dissolve about 0.0015 gm. of the salt at  $18^\circ \text{C}$ ., while its solubility in hydrochloric acid or in weak brine is very considerably greater than this. Thus, if a weight of pure silver to give, theoretically, 0.5 gm. of the chloride is dissolved in nitric acid and precipitated by the addition of a solution of common salt, there might be left unprecipitated in the liquor 0.002 gm. of the chloride and another 0.001 gm. might be dissolved by the wash-water. Therefore the weight of the chloride found would be 0.497 gm.

Moreover, if a weight of silver to give only 0.2 gm. of the chloride is taken, the solution errors would be nearly the same, and 0.197 gm. would be found. These solution errors may be considerable; it is extremely difficult to allow for them by calculations based on data obtained from solubility tables.

Two other frequent causes of error are adsorption and variation in composition of the precipitate. In the first case, the precipitate adsorbs some of the precipitant or other compound present in the solution. In the second case, two or more chemical compounds are formed by adding the precipitant to the solution to be analysed. For example, when a solution of potassium ferrocyanide is added to a solution containing zinc, the precipitate may be a mixture of  $K_2Zn_3Fe_2C_{12}N_{12}$  and  $Zn_2FeC_6N_6$ . The exact composition of this mixture depends on various factors—temperature, concentration of solution, rate of addition of ferrocyanide, other ions present in solution, etc. By a correct choice of the conditions, adsorption and variation of composition can usually be avoided. By working a blank in parallel with the assay under rigidly controlled conditions, most errors are minimised.

The methods in this section give fairly accurate results when the ordinary gravimetric errors are disregarded, but for special work it is essential to run a blank of approximately the same composition as the assay. For example, the percentage of silver in a coin has to be determined. Preliminary experiments have shown that the coin contains about 90 per cent. of silver, the remainder being copper. Take 0.4 gm. of pure silver and 0.044 gm. of copper and dissolve these metals in nitric acid. In a second vessel dissolve 0.444 gm. of the coin, using the same quantity of nitric acid. The two solutions will now be almost identical. To each add the same slight excess of a solution of common salt, adding the precipitant to each at the same rate and under the same conditions of temperature and stirring. Filter and wash both precipitates in exactly the same way.

Now 0.4 gm. of pure silver should yield, theoretically, 0.5315 gm. of chloride. Only 0.5298 gm. may have been collected from the blank and 0.5147 gm. from the coin. The calculation is as follows:

0.5298 gm. of silver chloride is obtained from 0.04 gm. of silver,

$$\therefore 0.5147 \text{ gm. of silver chloride is obtained from } \frac{0.4 \times 0.5147}{0.5298} \\ = 0.3886 \text{ gm. of silver.}$$

$\therefore$  0.444 gm. of coin contains 0.3886 gm. of silver.

$$\therefore \text{ In 100 gm. of coin is } \frac{0.3886 \times 100}{0.444} \\ = 87.52 \text{ gm. of silver.}$$

The calculation from the absolute weight of chloride obtained from the coin, neglecting the blank altogether, gives 87.30 per cent. of silver. The first result is obviously the more accurate.

**Note-book, Entries and Calculations.** A note-book of not less than quarto size will be found convenient for the entry of the results. The

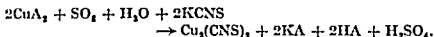
description and the results of the analytical process may be entered on the right-hand page, the left-hand page being reserved for the necessary calculations. Never jot down weighings and quantities on loose sheets of paper. A good plan is to keep a small note-book, little more than a pocket-book, in an outer pocket; this can be used for rough notes.

Calculations will be shortened by the use of the Table of Factors (p. 521). The symbol of the element (A) which is being determined will be found in the first column of this table. The formula of the compound (B) which has been precipitated and weighed is given in the second column. In the third is set out the ratio of the formula weights of A and B. In the fourth will be found the percentage of A and B, and in the fifth the logarithm of this percentage is given.

The first of the following determinations illustrates an entry suitable for a student's note-book:

### Determination of the Percentage of Copper in a Salt by the Thiocyanate Method

The information was given that the salt contained about 30 per cent. of copper and that those elements which interfered, namely, silver, lead, mercury, and all oxidising agents, were absent.



It is evident that 63.6 gm. of copper yield 121.6 gm. of precipitate. To obtain 0.8 gm. of precipitate (a suitable quantity), about 0.4 gm. of copper and, therefore, about 1.2 gm. of salt are needed. To obtain 0.8 gm. of precipitate about 0.6 gm. of KCNS is required.

About 1.2 gm. of the given salt was weighed out, using a weighing-bottle, and dissolved in a 400-ml. beaker in 200 ml. of water to which 2 ml. of dilute sulphuric acid had been added. Sulphur dioxide from a syphon was passed into the cold solution until the latter was saturated with the gas. Saturation was reached when a small bubble of the gas did not change in size on its way up through the liquid. About 0.7 gm. of KCNS was weighed out and dissolved in water. This solution was added to the copper solution slowly and with constant stirring. A green precipitate of cupric thiocyanate was first formed, but this soon became buff-coloured, almost white. The precipitate was allowed to settle and a few drops of KCNS solution were added to the clear liquid. There was no further precipitate.

Care was taken to use only slightly more than the required quantity of KCNS, because  $\text{Cu}_2(\text{CNS})_2$  is soluble in a solution of that salt.

The beaker was covered with a clock-glass and left overnight in a cupboard; the precipitate is slightly decomposed by light. Next morning the solution was again saturated with  $\text{SO}_2$ , the precipitate was allowed to settle, and the liquid was then decanted through a weighed sintered glass crucible. The precipitate was transferred to the crucible, and washed with cold water until the runnings no longer gave a red colour with ferric chloride. The final wash-liquor was 20 per cent. alcohol. The crucible was dried at  $115^\circ \text{C}$ . in an air-oven to constant weight.

**Results**

Weight of bottle and copper salt (1) = 7.4318 gm.

Weight of bottle and salt (2)         = 6.2547   ,,

Weight of salt taken = 1.1771   ,,

Weight of crucible = 7.6421   ,,

Weight of crucible and precipitate.

(Dried 1 hour)         = 8.2198   ,,

(Dried 1½ hours) = 8.2196   ,,

Weight of precipitate = 0.5775   ,,

Now 121.65 gm. of  $\text{Cu}_2(\text{CNS})_2$  contain 63.57 gm. of copper.
$$\therefore 0.5775 \text{ gm. of } \text{Cu}_2(\text{CNS})_2 \text{ contains } \frac{63.57 \times 0.5775}{121.65} \text{ gm. of copper.}$$

$$\therefore \text{In 1.1771 gm. of salt is } \frac{63.57 \times 0.5775}{121.65} \text{ gm. of copper.}$$

$$\therefore \text{In 100 gm. of salt are } \frac{63.57 \times 0.5775 \times 100}{121.65 \times 1.1771}$$

$$= 25.64 \text{ gm. of copper.}$$

(The salt supplied was pure copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and contained 25.45 per cent. of copper. Result was passed, but experimental errors should have tended to make it low, rather than high.)

*Note 2.* When antimony, tin or other salts which easily undergo hydrolysis are present, these may often be kept in solution by the addition of 3 gm. of tartaric acid dissolved in 30 ml. of water. The total volume of the solution should then be approximately 200 ml.

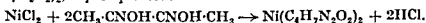
*Note 3.* The precipitate may be dealt with volumetrically (see p. 181).

*Note 4.* The best method for copper, the electrolytic method, is described on p. 228. Other methods, which are suitable for small quantities, are given on pp. 240 and 289.

**Determination of Nickel in its Soluble Compounds**

**The Nickel is precipitated by Dimethylglyoxime.**

When a neutral, or nearly neutral, solution of a nickel salt is treated with dimethylglyoxime, a red, crystalline, co-ordinated compound,  $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$ , is precipitated.



Weigh out accurately about 0.4 gm. of pure nickel ammonium sulphate,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , into a 500-ml. beaker and dissolve it in 200 ml. of water. Add a few drops of ammonia until the liquid (not the sides of the beaker) smells of ammonia. Heat to  $70^\circ \text{C}$ . and add carefully, with stirring, 60 ml. of a 1 per cent. solution of dimethylglyoxime in alcohol.

Let the beaker stand in a warm place for half an hour. Make sure that an excess of dimethylglyoxime has been added and also that the acid has not been produced in sufficient quantity in the reaction to make the solution acid. If necessary, add a few additional drops of ammonia.

Filter through a prepared Gooch, alundum, or sintered glass crucible. Wash with hot water. Dry at  $110^{\circ}$  to  $120^{\circ}$  C.

*Note.* Nickel in a pure, or almost pure, state is precipitated by dimethylglyoxime from ammoniacal solutions of copper, cobalt, zinc, and manganese, provided always that the concentration of the copper or cobalt is less than that of the nickel. It can also be precipitated from solutions containing iron and aluminium, provided enough tartaric acid is present to keep these metals in solution when ammonia is added, and provided all the iron is in the ferric state.

The glyoxime precipitate does not form properly in acid solution or in strongly ammoniacal solution. It is somewhat soluble in alcohol, and in no case should more than one-third of the liquid from which the nickel is being precipitated be alcohol; but a considerable excess of the glyoxime over that required theoretically for the precipitation of the nickel should be used.

The precipitate readily sublimes unchanged at  $250^{\circ}$  C. If necessary, it can be ignited rapidly and the nickel weighed as NiO.

In the presence of considerable quantities of zinc, manganese, or cobalt, nickel is best precipitated in acetate solution as follows: The solution should contain not more than 0.1 gm. of total metals and 0.5 ml. of  $H_2SO_4$  or HCl

The electrolytic determination of nickel is described on p. 231, and the salicylaldoxime method on p. 289.

#### Determination of Cobalt in Solution by $\alpha$ -Nitroso- $\beta$ -Naphthol

*Reagent.* Dilute pure acetic acid to twice its volume and then dissolve in it enough  $\alpha$ -nitroso- $\beta$ -naphthol to give a 2 per cent. solution. Heat is necessary. The solution must be freshly made.

*Procedure.* To a solution of the chloride or sulphate containing 5 ml. of concentrated hydrochloric acid and not more than 0.1 gm. of cobalt in 200 ml., at  $50^{\circ}$  C., add, with continual stirring, 10 ml. of reagent for every 0.01 gm. of cobalt judged to be present. Continue the heating and stirring for ten minutes. Allow to settle, and test for complete precipitation with more reagent. Allow to stand for two hours, collect in a filter-paper, dry and ignite in a Rose's crucible (p. 48) at a temperature of approximately  $1,000^{\circ}$  C.

Then either complete the ignition at  $1,000^{\circ}$  C. in a stream of oxygen, cool in oxygen and weigh as  $Co_2O_3$ ; or pass pure, dry hydrogen into the crucible at a dull red heat for fifteen minutes, so reducing to metal, cool in hydrogen and weigh. In either case the treatment must be repeated to constant weight. The second method is advised, because the " $Co_2O_3$ " is often a complex mixture of oxides.

Alternatively the precipitate may be collected in a Gooch crucible, transferred to an ordinary crucible and ignited at a high temperature. The oxides are then dissolved in hydrochloric acid and the cobalt is determined electrolytically (p. 231). In any case it is of little use to weigh the original precipitate after drying it at a low temperature because the cobalt salt,  $[C_{10}H_7O(NO)]_2Co$ , nearly always carries down with it a considerable quantity of the precipitant.

Copper and iron are quantitatively precipitated by this method. They must either be removed first, or determined in the mixture of ignited oxides or reduced metal. If twice as much nickel as cobalt is present, the ignited precipitate should be dissolved in hydrochloric acid and the cobalt reprecipitated. Pb, Hg, Cd, As, Sb, Al, Mn, Ca, or Mg do not interfere.

The  $\alpha$ -nitro- $\beta$ -naphthol reagent provides a sensitive test for cobalt. One drop of the neutral or slightly acid solution suspected of containing cobalt is dropped on to a filter-paper and covered by a drop of the reagent. A brown spot indicates cobalt. Sensitivity 1 : 1,000,000. Cu, Fe and relatively large proportions of Ni interfere.

### Determination of Iron in its Soluble Compounds

The Iron is precipitated as Ferric Hydroxide ; this is ignited and weighed as Ferric Oxide,  $\text{Fe}_2\text{O}_3$ .

Weigh accurately about 0.5 grm. of ferrous ammonium sulphate,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , into a 500-ml. beaker. Dissolve the salt in about 200 ml. of distilled water containing a few millilitres of dilute hydrochloric acid. Heat this solution, neutralise it with ammonia, and add 5 ml. of concentrated ammonia in excess. This procedure is necessary to prevent the formation of basic salts. Now add a solution of hydrogen peroxide in excess, and boil carefully for ten minutes to complete the oxidation and to granulate the precipitate. The solution of hydrogen peroxide used must be free from organic compounds.

Wash the precipitate twice by decantation with hot water, and collect it on a filter-paper. Continue the washing with hot water until the filtrate gives no precipitate with  $\text{BaCl}_2$  solution. Dry the precipitate in a steam-oven, and then transfer it to a crucible. Ignite with the paper at a bright red heat over a Bunsen flame to constant weight, and weigh as  $\text{Fe}_2\text{O}_3$ . As the burnt coal gas must not be allowed to react with the precipitate, the crucible must either be heated at an angle or inserted in a hole in an asbestos sheet.

It is usually much more convenient to determine iron by one of the many available volumetric methods (pp. 155, 179, 187).

### Determination of Aluminium in Solution

The Aluminium is precipitated by Ammonium Hydroxide as Aluminium Hydroxide : this is converted into Oxide,  $\text{Al}_2\text{O}_3$ , by ignition, and is weighed as such.

Weigh out accurately about 0.6 grm. of pure recrystallised potassium alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , into a 500-ml. beaker. Dissolve the salt in 100 ml. of water, add 25 ml. of a 10 per cent. solution of ammonium chloride, a few millilitres of dilute hydrochloric acid and a few drops of methyl red as indicator. Heat to boiling, and then add ammonium hydroxide slowly until the solution is distinctly yellow. Boil for two minutes and add ammonia drop by drop, with constant stirring, until the solution just smells of ammonia.

Wash the precipitate by decantation with a hot, 2 per cent. solution of ammonium nitrate, and transfer it to a filter-paper. Continue the washing of the precipitate on the paper with the hot ammonium nitrate solution until the filtrate is free from sulphate. Ignite the precipitate and paper wet in a platinum crucible, being careful to heat the crucible slowly at first and from the top. Finally, expose it to a white heat over the blowpipe flame. The crucible must be kept covered as much as possible because, on heating, the oxide may recrystallise and jump about in the vessel. Repeat the ignition until the weight becomes constant.

Freshly-ignited alumina is extremely hygroscopic. It is therefore somewhat difficult to weigh, and weighing should be carried out as rapidly as possible.

*Note.* If the hydroxide is not precipitated slowly, it may come down in such a form that it is almost impossible to collect and wash it. A soluble form of aluminium hydroxide exists, and there is always a tendency for the precipitate to change over to this soluble form. This is to some extent prevented by the presence of ammonium nitrate in the washing water. Complete precipitation can only be obtained in the first place in the presence of large quantities of ammonium salts. If a precipitate is very gelatinous and will not filter properly, repeat the determination or use the method given below.

### Determination of Aluminium with 8-Hydroxyquinoline (Oxine)

8-Hydroxyquinoline,  $C_8H_7ON$ , forms insoluble co-ordinated compounds with certain metals, notably with magnesium, zinc and aluminium. These compounds are characterised by their definite constitution and crystalline nature. They are therefore comparatively easy to handle.

The solution should be slightly acid with a mineral acid and should not contain more than 0.02 gm. of aluminium per 100 ml. The 8-hydroxyquinoline should be dissolved in 2N. acetic acid to make a 2 per cent. solution.

Heat the aluminium solution to  $60^\circ C$ . and add a 20 per cent. excess of the reagent. Add, with constant stirring, a solution containing 270 gm. of hydrated sodium acetate per litre until a permanent precipitate forms, and then 25 ml. more. After the precipitate has settled, collect it in a Gooch crucible, wash with cold water, dry at  $130^\circ C$ . and weigh as  $Al(C_8H_6ON)_2$ . The precipitate can also be analysed volumetrically (p. 171).

**Determination of Aluminium as Phosphate.** To determine small quantities of aluminium, especially in the presence of iron, it is better to precipitate as  $AlPO_4$ , which contains a smaller percentage of aluminium than does the oxide.

To the nearly neutral solution rather more than a ten-fold excess of  $(NH_4)_2HPO_4$  crystals is added. If a precipitate forms it is just cleared with dilute  $HCl$ , and the solution is diluted to 400 ml. Then 10 gm. of sodium thiosulphate in solution and 20 ml. of acetic acid are added. The solution is boiled for at least half an hour. The removal of the mineral acid takes place, and the aluminium phosphate is precipitated. The iron is reduced to the ferrous state, and is not precipitated.

As the aluminium phosphate is somewhat indeterminate in composition, the results given by this method are not accurate. However, as only small quantities of aluminium are being determined, the errors are probably smaller than those inherent in other processes.

### Determination of $SO_4$ in a Soluble Sulphate

The  $SO_4$  is precipitated as  $BaSO_4$ , and is weighed as such.

Weigh out about 0.5 gm. of pure recrystallised  $CuSO_4 \cdot 5H_2O$  into a 500-ml. beaker. Dissolve this in about 300 ml. of distilled water containing 4 ml. of concentrated  $HCl$ , and heat the solution to boiling.

To the boiling  $CuSO_4$  solution add a slight excess of a hot 3 per cent.  $BaCl_2$  solution. Stir the liquid and do not add the precipitant at a faster rate than 1 ml. per minute, in order to prevent the chloride from being



carried down with the sulphate. Allow the beaker to stand on a water-bath for half an hour. When the precipitate has settled, add a few drops of  $\text{BaCl}_2$  solution to the clear liquid to make sure that an excess has been added. Pour off the supernatant liquid through a filter, taking care not to disturb the precipitate. Wash the precipitate twice by decantation with boiling water. Finally, transfer it to the filter, and continue the washing with boiling water until the last few drops of the washing water give no turbidity with  $\text{AgNO}_3$  solution.

Dry the filter with the precipitate in a steam-oven. Detach the precipitate from the paper and transfer it to a crucible, preferably of platinum. Burn the paper in a platinum coil (p. 52) and put the ash into the crucible, as far as possible from the precipitate. Ignite the precipitate and the filter-ash together for about fifteen minutes at a dull red heat and allow the crucible to cool.

Any  $\text{BaSO}_4$  which is left adhering to the filter-paper may be reduced to  $\text{BaS}$  when the paper burns. If  $\text{BaS}$  is produced in any appreciable quantity, the weight of the precipitate will be too low. The  $\text{BaS}$  in the filter-ash should therefore be converted into  $\text{BaSO}_4$  as follows :

The filter-ash, which has been placed in a separate part of the crucible, is moistened with 2-drops of dilute  $\text{HCl}$ , and a drop of dilute  $\text{H}_2\text{SO}_4$  is added. The contents of the crucible are then heated very gently on a sand-bath until the liquid has been evaporated, great care being taken to avoid loss by spitting. The crucible and its contents are finally ignited at a dull-red heat and are weighed after they have been allowed to cool.

*Note 1.* When nitrates or chlorates are present, barium nitrate or chlorate is formed and this is carried down with the precipitate of barium sulphate. Since these salts cannot be removed completely from the  $\text{BaSO}_4$  by washing, the nitric or chloric acid must be removed by evaporation with  $\text{HCl}$  before the sulphate is precipitated by  $\text{BaCl}_2$ .

Certain metals, especially trivalent metals, also tend to be precipitated with the  $\text{BaSO}_4$ , and they should be removed by suitable precipitants before the

be purified in the following way from co-precipitated substances. Moisten the precipitate in the crucible with a few drops of dilute hydrochloric acid, warm gently on a sand-bath, and filter. Repeat this operation several times, adding the filter-ash to the precipitate, and ignite and weigh again.

*Note 3.* Certain authorities recommend a Gooch or alundum crucible for the collection of the  $\text{BaSO}_4$ . For this analysis, however, the method described above is probably still the best.

If a Gooch crucible is used, the sulphate is precipitated as before and is collected in the crucible. The precipitate is washed with hot water and may be dried in an air-oven at  $130^\circ \text{C}$ . or over. As such a process tends to give a loss of precipitate, the Gooch crucible on a sand-bath is better, in a muffle, or the Gooch crucible

that they are of a grade fine enough to retain the precipitate.

#### Determination of $\text{SO}_4$ in an Insoluble Sulphate

If the Sulphate is Insoluble in Water and in Acids it must be decomposed by fusion with alkali carbonates as follows :

Weigh out accurately about 0.1 gm. of pure, finely-powdered anhydrous  $\text{CaSO}_4$ , or gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), or plaster of Paris ( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ), into a platinum crucible, and add to it about 3 gm. of finely-powdered fusion mixture, made by mixing together equal weights of sodium and potassium carbonates.   
 glass rod rounded  
 n flame, the size  
 Keep in gentle

Cool the crucible by taking it out of the flame and swinging it round in small circles in such a way that the melt mounts up the sides. If this is done with skill the surface of the frozen salts is then U-shaped instead of plane. When

mass can be readily detached from its interior by a glass rod. The water may be heated if necessary.

Remove the crucible from the water by a clean pair of tongs, and carefully rinse it out into the solution with distilled water. Crush any solid particles which remain, filter the liquid, and wash the undissolved  $\text{CaCO}_3$  on the filter with boiling water, until the washing water is neutral. Mix the filtrate with the washings, add 2 drops of methyl orange and run in dilute  $\text{HCl}$ , guarding against loss by effervescence, until the solution turns pink. Then add a further 1 ml. of concentrated  $\text{HCl}$  for every 300 ml. of solution, and precipitate the sulphate as  $\text{BaSO}_4$  from the acidified solution, as is directed above.

#### Determination of Barium in its Soluble and Insoluble Compounds

The Barium is precipitated from solution as Barium Sulphate, and is weighed as such.

This analysis is the converse of the determination of sulphates. It can be carried out in exactly the same way, using 0.1 gm. of pure, recrystallised barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in the exercise. An excess of dilute sulphuric

Barium Compounds, which are Insoluble in Acid, are first fused with alkali carbonates. The barium carbonate residue, which is left on the filter when the fused mass has been treated with water, is washed and transferred to a beaker.   
 glass rod, and

to dissolve  
 The filter is  
 in is finally

#### Determination of Strontium

The Strontium is precipitated from solution as Strontium Sulphate, and is weighed as such.

Weigh out accurately about 0.5 gm. of pure precipitated strontium carbonate,  $\text{SrCO}_3$ , into a covered 300-ml. beaker. Dissolve the carbonate in a little dilute  $\text{HCl}$ , and add about 50 ml. of distilled water. Add dilute sulphuric acid in excess to this solution. In the beaker, let stand twelve hours; the washings g pure alcohol, described under the ignition of  $\text{BaSO}_4$ .

### Determination of Sulphur in Sulphides

The Sulphide is converted by a Suitable Oxidising Agent into Sulphate, and the Sulphate is precipitated and weighed as Barium Sulphate.

The choice of oxidising agent depends on the nature of the sulphide to be oxidised. Four methods are described below. The first is specially applicable to soluble sulphides, but the other three are used for insoluble sulphides.

**Oxidation by Bromine.** Weigh out accurately about 0.5 gm. of the finely-ground sulphide (see p. 254) into a 400-ml. beaker, and add 10 ml. of a mixture containing 2 parts of bromine and 3 parts of carbon tetrachloride by volume. Both these reagents must be free from sulphur. Allow the covered beaker and its contents to remain at room temperature for fifteen minutes, but with occasional shaking. Add 10 ml. of concentrated  $\text{HNO}_3$  and again shake the mixture occasionally during a further fifteen minutes. Then heat slowly and at a comparatively low temperature until the action is apparently over. When most of the bromine has disappeared, remove the cover and evaporate to dryness. Add 10 ml. of concentrated  $\text{HCl}$  and again evaporate to dryness to remove all nitric acid. Bake on a hot plate at a comparatively low temperature to dehydrate any silica. This temperature must be kept low, because there may be bisulphates present which are easily decomposed with loss of  $\text{SO}_2$ . Then treat the residue with 1 ml. of  $\text{HCl}$  and 100 ml. of hot water, and heat until all the sulphate is in solution. Filter into a 400-ml. beaker, washing twice with cold water and twice with hot. In the absence of a large quantity of iron, the sulphate, after the addition of enough  $\text{HCl}$ , can now be precipitated as  $\text{BaSO}_4$ .

If iron is present in considerable quantity, it will interfere and must be removed. Add ammonia to the silica-free filtrate, with stirring, to prevent the formation of iron hydroxide. The beaker and its contents are kept near  $70^\circ \text{C}$ . for the iron precipitate to settle. The two filtrates are then combined, and the usual precipitation with  $\text{BaCl}_2$  is carried out.

During these operations the volume of the filtrate is not to become very large. As  $\text{BaSO}_4$  is precipitated from solutions of the filtrate, the volume of the filtrate is reduced.

**Oxidation by Potassium Nitrate.** Weigh accurately about 0.5 gm. of very finely-powdered sulphide, and mix it in a large nickel crucible with ten times its weight of anhydrous sodium carbonate and twice its weight of finely-powdered potassium nitrate. Cover the mixture with a thin layer of sodium carbonate. Heat the crucible, very gently at first, until the contents are molten. Keep them molten for fifteen minutes. Cool, while swinging the crucible (p. 67), but do not plunge it into water. When cold, dissolve the melt in water, filter into a large porcelain dish, and boil the residue with dilute  $\text{Na}_2\text{CO}_3$  solution which must be free from sulphate. Filter again, and wash the residue until the washings are no longer alkaline. Add them to the first filtrate, neutralise with  $\text{HCl}$ , taking care not to lose liquid by effervescence, and evaporate to dryness. To remove all nitric acid, add 10 ml. of concentrated  $\text{HCl}$ , and

again evaporate to dryness. Dissolve the residue in 300 ml. of water containing 4 ml. of concentrated  $\text{HCl}$ , filter to remove silica if necessary, and precipitate the sulphur as  $\text{BaSO}_4$  (p. 65).

*Note.* As coal gas contains sulphur, the contents of the crucible may take up sulphur from this source. If a muffle furnace is not available, the simplest method of overcoming this difficulty is to place the crucible in a hole in a soft sheet of asbestos. The asbestos then acts as a shield.

**Oxidation by Nitric Acid.** Weigh out accurately about 0.5 gram. of very finely-powdered sulphide into a 300-ml. flask. Introduce a small funnel into the neck of the flask to prevent loss by spitting during dissolution, and carefully pour over the powder 10 ml. of a mixture of 3 parts of concentrated  $\text{HNO}_3$  and 1 part of concentrated  $\text{HCl}$ . When the powerful action of the acid has somewhat abated, heat the flask on a water-bath until the sulphur, which may separate at first, has dissolved. If the sulphur persists, it may be oxidised by the addition of a few millilitres of bromine water or of a small crystal or two of potassium chlorate.

Then carefully transfer the liquid to a porcelain dish, add a little sodium chloride to convert the free sulphuric acid into non-volatile sodium sulphate, and evaporate the liquid to dryness on the water-bath.

To ensure that all nitric acid has been removed, add 1 ml. of concentrated hydrochloric acid and 100 ml. of water. Make sure that all solid salts are wetted with this mixture, and again evaporate to dryness. If necessary, remove the silica and iron as directed under "Oxidation by Bromine" and then precipitate as  $\text{BaSO}_4$ .

**The Sulphide is converted into Ferrous Sulphide and the Sulphur oxidised to Sulphuric Acid by Hydrogen Peroxide.**

Weight out accurately about 0.5 gram. of the sulphide and mix it in a small hard-glass test-tube with 3 gram. of iron powder which has previously been heated in hydrogen, for instance in a Rose crucible (p. 48). Cover the mixture with a layer of iron powder. Now displace all air from the tube by a stream of pure, dry carbon dioxide. Heat the tube carefully, maintaining a slow stream of gas at a dull red heat for ten minutes. Cool in an atmosphere of carbon dioxide. If this experiment is carried out carefully, the sulphides are rendered soluble in acids. Iron pyrites is also converted quantitatively into ferrous sulphide.

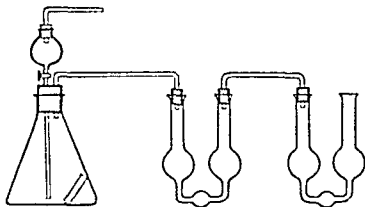


FIG. 60. DETERMINATION OF SULPHUR.

Transfer the tube and its contents to a flask (Fig. 60), which is connected up with two U-tubes, each partly filled with a solution

containing equal volumes of "20-volume" hydrogen peroxide and of dilute ammonia solution. Pass a stream of hydrogen through the apparatus, by way of the dropping-funnel, to displace air. The hydrogen must first have been freed from sulphur by passing it through either a solution of  $\text{AgNO}_3$ , or a solution of lead in sodium hydroxide.

Now add water to the flask until the tube is filled. Then slowly run in concentrated hydrochloric acid. Warm the flask to complete the reaction. When the action appears to be over, gently boil and pass a slow stream of hydrogen for fifteen minutes.

The sulphide is decomposed by the acid, and the hydrogen sulphide produced is carried over to the tubes containing the hydrogen peroxide, where it is partially oxidised.

Now wash out the contents of the two U-tubes into a beaker, and heat slowly to boiling to complete the oxidation of the sulphur to sulphuric acid and to decompose the excess of hydrogen peroxide. Precipitate the sulphuric acid as barium sulphate (p. 65).

If the original sulphide was soluble in dilute acid, it can be put directly into the reaction flask, the preliminary heating with powdered iron being omitted.

Instead of collecting the sulphuretted hydrogen in hydrogen peroxide, it can be collected in cadmium sulphate solution and determined volumetrically (p. 168).

#### Determination of $\text{SO}_3$ in a Sulphite or Thiosulphate

The Sulphite or Thiosulphate is converted into Sulphate by the addition of Bromine Water, and is determined as Barium Sulphate,  $\text{BaSO}_4$ .

Weigh out accurately about 0.5 gm. of crystallised sodium sulphite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , into a 500-ml. beaker. Dissolve the salt in water, and add

$\text{BaSO}_4$ , all hydrogen peroxide must be destroyed by boiling.

Volumetric Processes, which are much more convenient and rapid than the gravimetric processes for the determination of sulphites and thiosulphates, are given on pp. 169 and 182.

#### Determination of Calcium in its Soluble Compounds

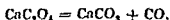
The Calcium is precipitated from the solution of the calcium salt as Calcium Oxalate, which is converted either into Carbonate or into Oxide, or is weighed as  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (see also p. 188).

Weigh put accurately into a 500-ml. beaker about 0.5 gm. of precipitated calcium carbonate, or of Iceland spar. Pour in some water, and gradually add dilute hydrochloric acid in quantity sufficient to dissolve the carbonate, guarding against loss by effervescence. Dilute this solution with water until its volume is about 100 ml.

Heat the liquid nearly to boiling. Then add a slight excess of a solution of ammonium hydroxide, boil and finally add a boiling solution of

ammonium oxalate slowly, in moderate excess. Allow the liquid to stand until the precipitate has settled, preferably overnight. Then pour off the liquid through a filter, taking care not to disturb the precipitate. Wash the precipitate in the beaker two or three times by decantation with hot water in which a small quantity of ammonium oxalate has been dissolved. Finally transfer the precipitate to a filter-paper by means of a glass rod tipped with rubber tubing, and using a wash-bottle with a fine jet. Wash the precipitate on the filter with a very dilute, hot solution of ammonium oxalate, until the last few drops of the washing water, after being acidified with  $\text{HNO}_3$ , no longer react with silver nitrate solution. Then dry in the steam-oven.

**Conversion of the Calcium Oxalate into Carbonate.** The precipitate is transferred, as completely as possible, to a platinum crucible. The filter-paper is burnt in a platinum-wire spiral (p. 52) and the ash is allowed to drop into the crucible. The crucible is then covered with a lid and is heated very gently at first; it is finally heated for about twenty minutes to a temperature sufficient to cause the bottom of the crucible to appear faintly red when it is shaded from direct light.



The crucible is weighed, after it has been allowed to cool in a desiccator.

After the crucible has been weighed the precipitate should be moistened with ammonium carbonate solution, which is then removed on a water-bath. The contents of the crucible are then heated cautiously to a low red heat until no more ammonium carbonate fumes are evolved. The ammonium carbonate reagent should volatilise without solid residue when it is heated alone. These operations must be repeated until the weight no longer increases, so that any oxide formed during the original ignition will be converted back to carbonate.

Alternatively, the crucible is covered by a Rose's lid and a slow stream of pure  $\text{CO}_2$  is led over the carbonate. If this is done, a higher ignition temperature is permissible.

**Conversion of the Calcium Carbonate into Oxide.** If the weight of the calcium carbonate obtained from the oxalate does not exceed 1 gm., the above result may be checked by weighing the calcium as oxide. Indeed, if the original precipitate is small, the oxalate may with advantage be converted directly into oxide, and be weighed as oxide instead of as carbonate.

In order to convert the calcium carbonate into oxide, the crucible and its contents are heated at bright redness for fifteen minutes; they are then allowed to cool, and are weighed. The crucible is once more heated for five minutes in the same way, and is weighed again. These operations must be repeated so long as the crucible and its contents lose weight. Remember that  $\text{CaO}$  is hygroscopic.

**Weighing as Calcium Oxalate.** A quicker, though less satisfactory, method for the determination of calcium is to collect the precipitated oxalate in a Gooch crucible. In this case, the precipitation and washing are carried out exactly as before, except that the precipitate is finally washed twice with pure, hot water. The crucible is dried at  $100^\circ$  to  $105^\circ \text{C}$ . The composition of the precipitate approximates to  $\text{CaC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

*Note.* If the calcium is to be weighed as carbonate or as oxalate, the oxalate may be collected in an alundum crucible; this is inadvisable if the carbonate is to be converted to oxide.

All other metals, except the alkali-metals and magnesium, are precipitated

titrate with a weak solution of ammonia, using methyl orange as indicator, until a distinct yellow coloration results.

If the concentration of magnesium is much higher than that of the calcium, some magnesium will be precipitated, despite these precautions. In this case the oxalate should be dissolved in dilute HCl and reprecipitated.

#### Determination of $\text{C}_2\text{O}_4$ in a Soluble Oxalate

The Oxalate is precipitated as Calcium Oxalate, either in neutral solution or in a solution containing acetic acid. The Calcium Oxalate is then ignited and is weighed either as Carbonate or as Oxide.

calcium, or collect it in a Gooch crucible, dry it at  $100^\circ$  to  $105^\circ$  C. and weigh it as  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .

A Volumetric Method for determining oxalate is given on p. 157.

#### Determination of Chlorine in a Soluble Chloride

##### The Chlorine is precipitated as Silver Chloride

Weigh out accurately about 0.3 gm. of pure sodium chloride, and dissolve this in about 100 ml. of cold water in a 500-ml. beaker. Add to the cold solution a few millilitres of dilute nitric acid, and then a slight excess of hot 2 per cent. silver nitrate solution. Shield the precipitate from daylight as much as possible during the whole of the procedure, since AgCl darkens in the light and suffers slight decomposition and loss of weight during this change. Heat the liquid in the beaker for some time, and finally boil it to flocculate the small particles of AgCl.

Wash the precipitate in the beaker three times by decantation with hot water containing a few millilitres of nitric acid; then collect it in a filter-crucible, continue the washing with water acidified with  $\text{HNO}_3$ , and then with hot water only. The washing may be considered to be finished when the addition of a drop of hydrochloric acid to the last few drops of the washing water produces only a very faint turbidity. To hasten drying, wash once with alcohol before disconnecting from the pump. Dry, first in the steam-oven, and then at  $130^\circ$  C., to constant weight.

*Note.* Heavy metals present in the solution may form basic chlorides and should therefore be removed by precipitation with a suitable reagent. The silver chloride is very liable to adsorb other salts, particularly silver nitrate, which may be present in solution. It is therefore important to use only a small excess of the  $\text{AgNO}_3$ .

The recovery of silver from these precipitates is described on p. 105.

#### Determination of Bromine and Iodine in Soluble Bromides and Iodides

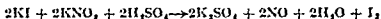
The procedure for the determination of these elements is exactly the same as that for chlorine. Sodium bromide or potassium iodide is a suitable salt for trying out the method.

Volumetric Processes for the determination of the halogens are described on p. 194.

### Determination of Chlorides and Iodides when Present Together

The total halogens are determined as silver halides, and then the iodine is removed with a fresh portion of the solution. The chlorine is again precipitated as  $\text{AgCl}$  and weighed as such.

A good way of removing the iodine is to treat the acidified solution with potassium nitrate.



Nitrous acid will not oxidise hydrochloric acid in very dilute solution.

Dissolve the mixture in 600 ml. of water in a litre beaker. Then add 3 ml. of dilute sulphuric acid and 1 gm. of potassium nitrite, which must be free from halides. Boil the solution, or bubble clean air through the hot solution, until it is entirely colourless. Then precipitate the chloride as  $\text{AgCl}$  in the usual way.

#### Determination of $\text{ClO}_2$ in a Soluble Chlorate

The Chlorate is converted by a suitable Reducing Agent into Chloride, and is determined as Silver Chloride.

Weigh out accurately about 0.3 gram. of pure recrystallised potassium chlorate,  $\text{KClO}_3$ , into a 500-ml. beaker. Dissolve the salt in about 100 ml. of water, and add 50 ml. of a 10 per cent. solution of ferrous sulphate crystals. Heat the liquid, with constant stirring, until it begins to boil, and boil for fifteen minutes. Then allow the liquids to cool and add nitric acid until the precipitated basic ferric salt is dissolved.

Precipitate the chloride (produced by the reduction of the chlorate) with silver nitrate, and collect and weigh the AgCl as described above.

Volumetric Methods for the determination of chlorates are given on pp. 152 and 176.

### Determination of $\text{ClO}_4^-$ in a Perchlorate

Perchlorates, unlike chlorates, are not reduced to chlorides by a ferrous salt. The solution containing the perchlorate is evaporated to dryness, and the residue is intimately mixed with five times its weight of ammonium chloride. The mixture is then heated slowly in a platinum crucible to a dull red heat. If necessary, the residue can be mixed again with ammonium chloride and again heated. A platinum crucible must be used, as platinum acts as a catalyst in the decomposition of the perchlorate. The chloride is then dissolved in very dilute nitric acid and determined as  $\text{AgCl}$ .

#### Determination of Cyanogen in a Soluble Cyanide

The Cyanogen is precipitated as Silver Cyanide,  $\text{AgCN}$ , and is weighed as such ; or the  $\text{AgCN}$  is ignited, and the residual  $\text{Ag}$  is weighed.

Collect and wash the precipitate in a Gooch or alundum crucible, and dry it at 105° C. in an air-oven until the weight is constant. From the weight of AgCN thus obtained, the percentage of cyanogen may be calculated.

Silver cyanide decomposes fairly easily. A check on the first result can therefore be obtained by heating the precipitate in a larger, uncovered crucible until the weight is constant. Repeated heatings may be necessary. Metallic silver is left after the expulsion of the cyanogen.

In preparing the crucible it is well to ignite it first at a red heat, and then to cool and weigh it. It should be then soaked in water, dried at 103° C., and weighed again. It is then possible to make a small correction for the change in weight of the crucible due to the two heat treatments.

*Note.* Commercial potassium cyanide is not pure, and varies in composition:



hence it will not yield the theoretical percentage weight of cyanogen corresponding with the formula KCN. In order to check the accuracy of the result obtained, it is necessary either to use chemically pure potassium cyanide or to make a duplicate determination of the cyanogen in the commercial salt.

A more satisfactory Volumetric Method for cyanide is given on p. 195.

### Determination of Silver in its Soluble Compounds

The Silver is precipitated as Chloride, and is weighed as such.

Weigh out accurately about 0.3 grm. of pure recrystallised silver nitrate,  $\text{AgNO}_3$ , and dissolve it in about 100 ml. of distilled water; then add a small quantity of dilute nitric acid.

Heat to boiling and slowly add dilute hydrochloric acid in slight excess, with constant stirring. The addition of another drop of HCl must not cause any further precipitate in the clear liquid from which the precipitate has subsided.

Allow the beaker to stand in a dark place until the precipitate has settled. Then decant the liquid, and wash the precipitate three times by decantation with boiling water containing a little  $\text{HNO}_3$ . Transfer the precipitate to a filter-crucible, and complete the washing with water acidified with  $\text{HNO}_3$ , and then with hot water only.

As soon as the  $\text{AgNO}_3$  test shows that the filtrate is free from chlorides, wash the precipitate once with alcohol, dry it in the steam-oven, and then at  $130^\circ \text{C}$ . to constant weight.

### Determination of Lead in its Soluble Compounds

**Determination of Lead as Lead Sulphate.** Weigh out accurately about 0.3 grm. of pure lead nitrate and dissolve the crystals in the least possible quantity of water in a porcelain dish. Cautiously add 10 ml. of concentrated  $\text{H}_2\text{SO}_4$ , and evaporate on a hot plate or on an iron pot (p. 36) until dense white fumes are produced. Cool, and dilute carefully with 30 ml. of water. Cool again, add 10 ml. of alcohol, and stir. Allow the precipitate to settle for three or four hours and then collect it in an alundum crucible. Wash it with 10 per cent. sulphuric acid, and finally with alcohol. Heat it slowly, and finally ignite it at a dull red heat to constant weight.

**Determination of Lead as Lead Chromate.** Weigh out accurately about 0.3 grm. of pure lead nitrate, dissolve it in 200 ml. of water and add acetic acid to the solution until it is distinctly acid. Heat, and to the hot solution add 4 per cent. potassium dichromate solution in slight excess. Continue the heating until the colour of the precipitate is a definite yellow. The supernatant liquid must also be coloured. Allow the precipitate to settle, filter it through a Gooch crucible, wash it with hot water and finally once with dilute alcohol. Dry at  $120^\circ \text{C}$ .

*Note.* The lead chromate is of a somewhat indefinite composition. Use the factor 0.6375, instead of 0.6411 the theoretical factor.

The chromate may also be determined volumetrically (pp. 154 and 172).

The Electrolytic Determination of lead as dioxide is given on p. 233.

### Determination of Zinc in its Soluble Compounds

The Zinc is precipitated as Carbonate and is weighed as Oxide.

Weigh out accurately about 0.5 gm. of pure recrystallised zinc sulphate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . Dissolve this in a 500-ml. beaker in about 150 ml. of water. Heat the solution nearly to boiling, and add sodium carbonate solution in a very slight excess. Boil for a short time; then allow the precipitate to settle, and wash it three times by decantation with boiling water; finally collect the precipitate in an alundum filter-crucible. The washing should be continued until the filtrate shows no alkalinity to litmus-paper, and gives no precipitate with  $\text{BaCl}_2$  solution.

Dry the precipitate in a steam-oven, and ignite it in a large, covered nickel crucible over a Bunsen flame. The precipitate should be heated at redness to constant weight. Care must be taken during the ignition to prevent unburnt gases from entering the crucible. Such gases would reduce the oxide to zinc, which would then be lost by volatilisation.

### Determination of Manganese in its Soluble Compounds

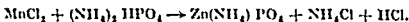
The Manganese is precipitated as Manganese Ammonium Phosphate and is weighed as Pyrophosphate.

Volumetric methods for the determination of manganese (p. 267) are to be preferred to the gravimetric methods on account of their greater speed and accuracy. The gravimetric method given below, however, yields excellent results.

As an exercise, an accurately-weighed quantity of potassium permanganate can be dissolved in a small quantity of dilute  $\text{H}_2\text{SO}_4$ . The permanganate is then reduced by  $\text{SO}_2$ , excess of  $\text{SO}_2$  removed by boiling, and the manganese sulphate determined as follows:

The solution should contain not more than 0.2 gm. of manganese in about 200 ml. of water. To this solution add 20 gm. of ammonium chloride and 2 gm. of  $(\text{NH}_4)_2\text{HPO}_4$ . Boil, and add hydrochloric acid, if necessary, until the solution is quite clear. Now to the boiling solution add a dilute solution of ammonia, very slowly and with constant stirring, until a precipitate begins to form. Boil until this precipitate becomes crystalline. Add a few more drops of ammonia, boil, add more ammonia, and so on until no further precipitate forms. Then add a further small quantity of ammonia. Stand the beaker in ice water to cool.

After two hours, filter through an alundum crucible, and wash with 10 per cent. ammonium nitrate solution, to which a few drops of ammonia have been added, until no chlorides remain. Dry and ignite very cautiously and gently at first, but finally at a bright red heat.



### Determination of Bismuth in its Soluble Compounds

The Bismuth is precipitated and weighed as Bismuth Phosphate,  $\text{BiPO}_4$ .

The solution containing the bismuth must be free from chlorides, which can be removed by evaporating twice to a syrupy consistency with nitric acid. The solution should also be concentrated, and not greater than 100 ml. in volume.

Add concentrated ammonia until a slight, permanent precipitate results. Dissolve this in 2 ml. of 30 per cent. nitric acid. To the boiling solution add, with constant stirring and from a burette, a five-fold excess of a 10 per cent. solution of diammonium hydrogen phosphate. Then dilute to 400 ml. with boiling water and almost boil for fifteen minutes. Collect the precipitate in a Gooch crucible, and wash it with 3 per cent. ammonium nitrate which has been slightly acidified with nitric acid. Dry, and ignite gently inside a large nickel crucible.

A suitable solution for practice can be obtained by igniting some pure bismuth oxide,  $\text{Bi}_2\text{O}_3$ , to constant weight. About 0.3 gm. of this is weighed out accurately and dissolved in dilute nitric acid.

### Determination of Magnesium in its Soluble Salts

The Magnesium is precipitated as Magnesium Ammonium Phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ; this is converted by ignition into Magnesium Pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , and is weighed as such.

Weigh out accurately about 0.5 gm. of pure recrystallised magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , into a 500-ml. beaker. Dissolve the salt in about 50 ml. of cold water, add a few millilitres of  $\text{NH}_4\text{Cl}$  solution, and then  $\text{NH}_4\text{OH}$  solution in moderate excess, since the phosphate precipitate is slightly soluble in pure water but is practically insoluble in water containing ammonia. If a precipitate forms when the  $\text{NH}_4\text{OH}$  solution is added, it must be redissolved by adding more  $\text{NH}_4\text{Cl}$  solution.

To the clear alkaline liquid add an excess of sodium phosphate solution (Note 1), and stir the liquid vigorously, rubbing the inside of the beaker with the rod, but without scratching the glass.

Allow the liquid to stand for twelve hours, and then filter it. This delay is recommended in order to ensure the complete precipitation of the double phosphate. But if the solutions are mixed in a stoppered vessel instead of in a beaker, and the mixture is at once vigorously shaken for five minutes, precipitation is complete in thirty minutes. If this method is used, it is better to precipitate with  $(\text{NH}_4)_2\text{HPO}_4$ . When a sodium salt is used, some  $\text{MgNaPO}_4$  may be precipitated at first. This salt changes on standing to the less soluble ammonium salt.

The precipitate is washed on the filter with  $\text{NH}_4\text{OH}$  solution, made by diluting one volume of  $\text{NH}_4\text{OH}$  solution, of 0.880 specific gravity, with three volumes of water. The washing must be continued until a few drops of the washing water, after being acidified with nitric acid, give no opalescence with silver nitrate solution.

The precipitate is now dried in a steam-oven, and is detached as completely as possible from the filter-paper and transferred to a platinum crucible. The filter is incinerated in a coil of platinum wire, by heating it at first very gently and finally exposing it to a red heat. The filter-ash (Note 2) is then dropped into the crucible.

The crucible is now covered with the lid, and is heated gently by a small flame for about ten minutes; it is then heated to redness, and finally to bright redness, in a flame hot enough to melt easily a piece of copper wire. It is then allowed to cool in a desiccator, and is weighed. The ignited precipitate should be perfectly white, and the ignition should be repeated until it ceases to lose in weight.

*Note 1.* Some authorities state that the addition of  $\text{NH}_4\text{OH}$  before the phosphate causes the formation of  $\text{Mg}_3(\text{PO}_4)_2$ , which remains unaltered when it is heated. The following procedure will prevent this: To the boiling solution, which must be neutral or slightly acid and free from ammonium salts, add sodium ammonium phosphate or microcosmic salt solution, drop by drop, until precipitation is complete. The greater part of the magnesium will now have been precipitated as  $\text{MgHPO}_4$ . Allow the solution to cool and add, with constant stirring, one-third of its volume of ammonia solution of 0.88 specific gravity. The amorphous precipitate will be at once changed into crystalline  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , and the magnesium still in solution will be thrown down in the same form.

*Note 2.* The ash should contain no particles of carbon, which may persist if the precipitate has been heated too strongly at first. The use of ammonium

*Note 3.* It is not advisable to use a special form of crucible in this determination because of the very high ignition temperature required. The alkaline phosphate solutions may react with the asbestos of a Gooch, so causing inaccuracy.

The Magnesium is precipitated with 8-Hydroxyquinoline and is weighed as  $\text{Mg}(\text{C}_8\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ .

For the preparation of the 8-hydroxyquinoline solution see under Aluminium (p. 65).

Make the solution of magnesium, which should not contain more than 0.02 gm. of metal in 50 ml., slightly alkaline with ammonia, after having added sufficient ammonium chloride to prevent the formation of a precipitate of magnesium hydroxide. Then heat to  $80^\circ$  to  $90^\circ \text{C}$ . and add, with stirring, a 5 per cent. alcoholic solution of the reagent in slight excess. The solution will then be slightly yellow. Next add 4 ml. of concentrated ammonia, stir continuously for ten minutes, allow to stand until the precipitate has settled, and collect it in a Gooch crucible. Wash it thoroughly with hot water, to which a small quantity of ammonia has been added, and dry it at  $105^\circ \text{C}$ . Alternatively, dry it at  $130^\circ$  to  $140^\circ \text{C}$ . to constant weight. In this case the water of crystallisation is lost. The latter method is to be preferred.

The precipitate can also be analysed volumetrically (p. 171).

The above method will separate small quantities of magnesium from the alkaline earths, but if much calcium is present the following procedure is recommended:

To the boiling solution, add 10 gm. of ammonium acetate and a few millilitres of ammonia; then quickly add ammonia until the solution is alkaline to phenolphthalein-paper. Filter at once, and wash with a 5 per cent. solution of ammonium acetate to which a few millilitres of ammonia have been added. Dissolve the precipitate in hot, dilute  $\text{HCl}$  and reprecipitate it as above. Collect the precipitate in a Gooch crucible and wash it with hot water containing a small quantity of ammonia.

A still better method is to precipitate the calcium as oxalate (p. 70) and then, without filtering, to precipitate the magnesium by the first method. The two precipitates are then collected and washed and the oxine compound is determined volumetrically.

### Determination of $\text{PO}_4$ in a Phosphate

The  $\text{PO}_4$  is precipitated as Magnesium Ammonium Phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ; this is converted into Magnesium Pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ .

Weigh out accurately about 0.3 gm. of pure potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , into a 500-ml. beaker, and dissolve the salt in about 100 ml. of water. Add a considerable excess of "magnesia mixture" (see below) to the solution, and clear with hydrochloric acid if necessary. Boil, and to the boiling solution add 0.880 ammonia diluted fifty times, until a precipitate forms. Continue to add the dilute ammonia very slowly until the liquid just smells of ammonia. Then, to the cooled solution, add one-fifth of its volume of concentrated ammonia. The precipitate will be ready to filter after half an hour. Treat the precipitate in the manner described above under the determination of magnesium as phosphate (p. 76).

*Note.* Because of the adsorptive properties of magnesium ammonium phosphate, the above process gives good results only when there are few other salts present in solution. If other salts are present the original magnesium precipitate should be dissolved in dilute hydrochloric acid and reprecipitated.

**Preparation of "Magnesia Mixture."** The Ministry of Agriculture and Fisheries has laid down the determination of phosphorus in magnesium chloride and ammonium chloride. Add 700 ml. of 8 per cent. ammonia solution and mix. Allow the solution to stand for not less than three days, and filter.

The 8 per cent. ammonia is to be made by diluting 0.880 ammonia with 3 volumes of water, and adding either concentrated ammonia or water until the specific gravity of the solution is 0.967.

The Phosphate is precipitated as Ammonium Phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , and is weighed as such, or is converted to Phosphomolybdic Anhydride,  $\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3$ .

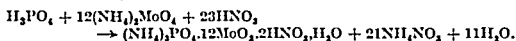
This method, though probably less accurate than the "magnesia" method given above, possesses three great advantages: (1) The phosphorus content of the precipitate is small, and therefore comparatively small quantities of phosphorus yield comparatively large precipitates. (2) As precipitation takes place in strongly acid solution, the method is suitable for the determination of the phosphate contents of salts which are insoluble in water but soluble in acids. (3) The phosphomolybdate is soluble in dilute ammonia. An accurate determination of an insoluble phosphate can therefore be made by first precipitating it as molybdate, dissolving this precipitate in dilute ammonia, and reprecipitating with "magnesia mixture" as described above. Few of the commoner elements are precipitated. The chief interfering elements are silicon, which must be removed by evaporating to dryness, redissolving the residue in acid and filtering; and arsenic, which is removed by reduction with  $\text{SO}_2$  and precipitation with  $\text{H}_2\text{S}$ .

The solution should contain not more than 0.1 gm. of  $\text{P}_2\text{O}_5$ , and should be some 100 ml. in bulk. Add 10 gm. of solid ammonium nitrate and 15 ml. of concentrated  $\text{HNO}_3$ , and heat nearly to boiling. Then run in a 3 per cent. solution of ammonium molybdate (see *Note*) through a filter-funnel, the stem of which has been drawn off so that the molybdate enters the phosphate solution slowly and in a fine stream. The molybdate solution should be as hot as possible, and the phosphate solution should be stirred. A considerable excess of the precipitant must be used.

Allow the precipitate to stand for one hour in a warm place, and then

filter it through an alundum or Gooch crucible. Wash it with a 1 per cent. solution of nitric acid until the runnings no longer turn a solution of potassium ferrocyanide brown, and finally with water. Dry it for two hours at  $110^{\circ}\text{C}.$ , and weigh it.

The reaction is as follows :



On drying at  $110^{\circ}\text{C}.$ , the phosphomolybdate loses the nitric acid and water.

In order to convert the precipitate to the anhydride, the crucible is placed on a pad of asbestos in a larger nickel crucible, which is nearly closed by a lid, and is heated by a small Bunsen flame. The yellow ammonium compound will lose ammonia, and it must be heated until it has become uniform bluish-black in colour. Care must be taken not to overheat the precipitate, because molybdic oxide sublimes very readily at a red heat. A suitable temperature will be obtained if the bottom of the nickel crucible is just red hot on the outside.

The original ammonium phosphomolybdate precipitate can be determined conveniently by a volumetric method (p. 136).

*Note.* The Ministry of Agriculture and Fisheries in the *Fertilisers and Food-stuffs Order* (1932) has laid down that ammonium molybdate solution made as follows shall be used in the determination of phosphates in manures: Put 125 gm. of molybdic acid and 100 ml. of water in a litre flask. Add 300 ml. of 8 per cent. of ammonia (made as directed under "magnesia mixture," p. 78)

#### Determination of $\text{AsO}_4$ in a Soluble Arsenate

The  $\text{AsO}_4$  is precipitated as  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ ; this is converted by ignition to  $\text{Mg}_3\text{As}_2\text{O}_7$ .

Weigh out accurately about 0.5 gm. of pure recrystallised sodium arsenate,  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , into a 500 ml. flask. Dissolve the salt in about 100 ml. Then add 10 ml. of 10 per cent. ammonia solution. Now add 10 per cent. ammonia solution from a burette until the solution is of a permanent red colour. Finally add one-third of its volume of 10 per cent. ammonia to the red solution and leave the precipitate to settle for one hour, or preferably overnight.

Collect the precipitate in a Gooch or alundum crucible and wash it with 2.5 per cent. ammonia until free from impurities. Dry it in a steam-oven, cover the precipitate with a thin layer of ammonium nitrate and heat it, slowly at first and finally to a bright red heat. The special crucible should have been placed in a larger nickel crucible. Then cool in a desiccator and weigh. Alternatively, instead of using ammonium nitrate, fit the crucible with a Rose's lid and ignite in

corresponding  
). The ignition  
latter.

#### Determination of Sodium in Sodium Chloride

The Sodium Chloride is converted into Sodium Sulphate,  $\text{Na}_2\text{SO}_4$ , by treatment with  $\text{H}_2\text{SO}_4$ , followed by evaporation and ignition.

This process can be applied to the determination of sodium in any compound which leaves only a residue of  $\text{Na}_2\text{SO}_4$  when it is evaporated with  $\text{H}_2\text{SO}_4$ .

Weigh out accurately about 0.5 gm. of pure sodium chloride into a platinum crucible. Dissolve the salt in as small a quantity of water as possible, and add concentrated sulphuric acid drop by drop, quickly replacing the cover of the crucible after each addition of acid. As soon as the whole of the salt has been acted upon, heat the crucible and its contents cautiously over a small Bunsen flame.

The crucible should be supported in an inclined position, and be almost covered by the lid, a small opening only being left to permit the fumes of the sulphuric acid to escape; and the heat should be applied near the top of the crucible, in order to prevent the liquid from creeping up the sides of the vessel (Fig. 52, p. 50).

White fumes should escape during heating, since they prove that  $H_2SO_4$  has been added in excess. The crucible should be heated to redness for at least fifteen minutes after the fumes have ceased to appear. It is then allowed to cool in a desiccator, and is weighed. The above processes should be repeated until there is no loss in weight after reheating for five minutes.

The salty mass becomes pasty during heating. This is due to the change of the sodium bisulphate, which is formed first, into the less fusible normal sulphate. This change may be accelerated by adding a small quantity of powdered ammonium carbonate to the cold crucible. The lid is then replaced, and the crucible is heated gently at first and then strongly for a few minutes. This treatment should be repeated until the weight of the crucible and its contents becomes constant.

The sodium in a solution of sodium salts . . . . .  
a portion of the solution nearly to dryness on  
porcelain evaporating dish. When room has  
solution is added; and so on. The final solution is then treated with sulphuric  
acid as described above.

**Precipitation as Sodium Uranyl Zinc Acetate.** The reagent is prepared by  
ate dihydrate,  
1 gm. of zinc  
water. After

separate, owing to the impurities present;  
sodium chloride. This ensures that the reagent  
precipitate. Filter the reagent ready for use.

Make the solution to be analysed approximately neutral, and dilute it so that 1 ml. contains 4 to 8 milligrams of Na. Mix 1 ml. vigorously with 15 ml. of the reagent, and after one hour at  $20^\circ C$ . filter the mixture on a weighed, sintered glass crucible. Wash the precipitate successively with seven 2-ml. portions of reagent at  $20^\circ C$ ., five 2-ml. portions of 95 per cent. alcohol (saturated with the

### Determination of Potassium in its Soluble Compounds

The potassium is weighed either as chloroplatinate, as perchlorate or as sulphate.

The Potassium Chloride is precipitated as the Double Chloride of Platinum and Potassium,  $K_2PtCl_6$ , and is weighed as such.

This method is only applicable to those potassium compounds which can be converted completely into potassium chloride by evaporation with hydrochloric acid, because it is only from a solution containing chlorides that potassium can be completely precipitated as  $K_2PtCl_6$  by chloroplatinic acid ( $H_2PtCl_6$ ).

Weigh out accurately into a porcelain dish (diameter, 10 cm.) about 0.25 gm. of pure recrystallised potassium chloride. Dissolve this in a small quantity of water, and add a few drops of hydrochloric acid. Then add platinum chloride solution in such quantity that the dish contains rather more than is required to react with all the alkali metals present. Evaporate the liquid slowly on a water-bath, until a syrupy liquid, which solidifies on cooling, is obtained. A common mistake is not to carry this evaporation far enough, but the solution should not be evaporated to dryness.

Now pour 80 per cent. alcohol on the residue. Gently shake the liquid round in the dish, so as to mix the contents uniformly together. Allow the precipitate to settle completely and pour off the liquid through a filter-crucible. Repeat these operations twice, or until the precipitate has a uniform golden-yellow colour, and finally transfer the undissolved double salt to the filter by means of a stream of liquid from a small wash-bottle containing alcohol.

Wash the precipitate on the filter with alcohol until the washings are no longer coloured; then dry the crucible and its contents at  $100^\circ C.$ , finally heating at  $135^\circ C.$  to constant weight. During the heating the crucible must be kept covered at first, because the crystals may decrepitate.

*Note.* When separating potassium from sodium by this method, it is necessary to remember that sodium chloride is insoluble and sodium chloroplatinate is soluble in 80 per cent. alcohol. It is therefore essential to add sufficient chloroplatinic acid to convert all the sodium as well as all the potassium to the chloroplatinate.

#### The $K_2PtCl_6$ is converted to Platinum and Weighed.

A check on the result obtained by the method given above can be made by reducing the double chloride to metallic platinum. The precipitate should have been collected in a sintered glass or alundum crucible. It is removed from the crucible to a large boiling-tube by washing with successive quantities of hot water. Add 4 ml. of concentrated  $HCl$  and a piece of pure magnesium weighing about 0.5 gm. to the hot solution. Stir the liquid and move the magnesium up and down the tube, using a glass rod which has been flattened at one end. When the action has ceased, add more hydrochloric acid and leave the tube in hot water in a beaker on a hot-plate for an hour. If reduction is complete the liquid should be quite colourless.

Collect the platinum on a filter-paper, wash it with hot water acidified with a little dilute hydrochloric acid, and ignite it in a porcelain or, preferably, a platinum crucible.

*Note.* A combination of these two methods serves for the determination of potassium in almost any mixture, except that potassium cannot be separated from ammonium salts by the use of chloroplatinic acid. Other chloroplatinates either are soluble in alcohol or are decomposed by it, or are insoluble both in alcohol and in boiling water. Thus, if a chloroplatinate is precipitated in the



presence of alcohol and is washed with that solvent, and then boiling water is passed over the precipitate on the paper, any platinum in the final filtrate must necessarily have been in combination either with potassium or ammonium.

The Potassium is precipitated as Potassium Perchlorate,  $\text{KClO}_4$ , by Perchloric Acid in the Presence of Alcohol.

This method is applicable in the presence of chlorides and nitrates of the alkaline earth metals, magnesium and the alkali metals, and also in the presence of phosphates, but ammonium salts and sulphates must be absent. Ammonium salts, if present, are removed by ignition, and sulphates by the careful addition of barium chloride solution.

For practice weigh out accurately about 0.3 gm. of pure potassium chloride, dissolve the salt in 20 ml. of hot water in a small unscratched glass dish, and, since 1 ml. of the 20 per cent.  $\text{HClO}_4$  solution converts 90 milligrams of potassium into perchlorate, add 5 ml. of 20 per cent.  $\text{HClO}_4$  solution. This is more than twice the  $\text{HClO}_4$  solution theoretically required to convert the potassium into perchlorate. Now evaporate on a water-bath, with stirring, to a syrupy consistency; add a small quantity of hot water and continue the evaporation on a hot plate, with constant stirring, until white fumes of  $\text{HClO}_4$  appear. If white fumes do not appear, add more water and  $\text{HClO}_4$  solution, until finally heavy fumes of  $\text{HClO}_4$  are obtained on evaporation. Cool. It is most important that the assay should be quite cold before alcohol is added, or there may be a most dangerous explosion. Then stir up the cool mass thoroughly with 20 ml. of alcohol, which has been distilled in the presence of potassium hydroxide and then saturated with solid potassium perchlorate, and break up the crystals somewhat to bring a large surface of solid into contact with the solvent.

At once decant the solution through a filter-crucible, which has been previously washed with a saturated solution of  $\text{HClO}_4$  in alcohol, dried at  $130^\circ \text{C}$ . and weighed. Finally, wash the precipitate by decantation with 15 ml. of the alcoholic solution of  $\text{HClO}_4$ , and transfer it to the filter; wash it in the crucible first with some of the alcoholic  $\text{HClO}_4$  solution, and finally once with pure alcohol; dry it at  $130^\circ \text{C}$ . and weigh.

*Note.* The crystals are heavy and difficult to see, even against a dark background. To ensure that all are transferred to the crucible, allow the dish to dry finally by evaporation, and carefully brush in any crystals.

**Determination of Potassium as Sulphate.** The process is exactly parallel to that described on p. 79 for sodium compounds. It is only suitable for those potassium compounds which leave pure potassium sulphate,  $\text{K}_2\text{SO}_4$ , when the residue left after evaporation with sulphuric acid has been ignited.

### Determination of Ammonium in its Compounds

The ammonia gas is driven off by heating the substance either with a solution of sodium hydroxide or with lime, and is determined either gravimetrically or volumetrically. The volumetric method (p. 133) is generally to be preferred.

The Ammonia is expelled by heating the Ammonium compound with a solution of Sodium Hydroxide, and is absorbed in dilute  $\text{HCl}$ ; the Ammonium Chloride thus produced is precipitated as the Double Chloride,  $(\text{NH}_4)_2\text{PtCl}_6$ , by Chloroplatinic Acid, and is weighed as such.

The General Description of the Method will be understood by reference to Fig. 61. The weighed ammonium compound is introduced into the decomposition-flask (*a*), and the sodium hydroxide solution is allowed to drop upon it from the dropping-tube (*b*). When the flask is heated, ammonia is evolved, and is absorbed by the dilute acid in the cooled absorption-flask (*h*). The absorption tube (*n*) contains pieces of broken glass moistened with dilute acid: this acid retains traces of ammonia which may have passed through the acid in the flask (*h*). The enlargement in the tube (*d*) receives any acid which may be sucked back from the absorption flask (*h*) and prevents it from entering the decomposition flask (*a*).

**Description of the Apparatus (Fig. 61).** A round 500-ml. flask (*a*) is fitted with a rubber bung through which passes a dropping-tube (*b*) of about 50 ml. capacity. The lower end of this tube is drawn out to a fine point. The flask is connected by means of a bent tube, carrying a bulb (*c*) and a rubber joint with a 50-ml. pipette (*d*). The connecting tube and the top of the pipette must be of the same diameter, and their ends must be brought into close contact within the joint. The pipette passes through a rubber stopper which is fitted in the neck of a 300-ml. conical flask (*h*). The lower end of the pipette is drawn out to a fine point. A small absorption tube (*n*), filled with broken glass, is also fitted into the same stopper.

The conical flask is filled to the depth of about half an inch with hydrochloric acid, made by diluting the concentrated acid with six times its volume of water. The acid, to which 2 drops of methyl orange have been added, is poured into the flask through the absorption tube (*n*) containing the broken glass, and the glass is thus wetted with the liquid. The point of the pipette is adjusted to dip just below the surface of the acid.

The whole apparatus should be screened, or placed in a fume cupboard, in order to shelter it from draughts while it is being used, because an intermittent air current may cause the distillation to be very irregular.

**Procedure.** About 1 gram. of pure crystallised ferrous ammonium sulphate,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is accurately weighed, all crystals which show a yellowish tinge being rejected. The salt is introduced into the round flask (*a*), and is then dissolved in about 50 ml. of water. Some small pieces of clean, porous porcelain are then added to minimise bumping when the solution is boiled, and the rubber bung carrying the funnel and trap is fitted into place. The bulb of the dropping-tube (*b*) is now filled with sodium hydroxide solution, prepared by dissolving 1 part of NaOH in 4 parts of water. The connection (*c*) with the receiver (*h*) is then made by means of the rubber joint, with a glass-to-glass connection inside the joint.

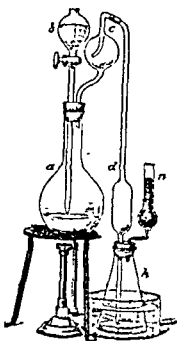


FIG. 61. DETERMINATION OF AMMONIA.

The contents of the round flask are now heated to gentle boiling, and the NaOH solution is allowed to drop slowly into the flask by slightly opening the stop-cock of the dropping-tube (b). As the ammonia gas is driven off, it is absorbed by the acid in the conical flask (h), which is kept cool by cold water in a dish.

The bulb-tube (c) stops any alkaline liquid spirting from the boiling solution. If the ammonia is driven over at all rapidly, the trap ceases to function efficiently. If the least trace of the concentrated sodium hydroxide finds its way into the flask (h), it will count as ammonia if the volumetric determination (p. 133) is used, and the results will be unreliable. The point of the pipette (d) must be always just immersed in the acid, because if a volume of acid greater than 50 ml. is drawn into the pipette some of it will be drawn back into the distillation-flask and the device will be worthless. The pipette must therefore be raised occasionally as the volume of liquid in the flask increases.

As soon as all the NaOH solution has flowed from the tube (b) into the flask, the stop-cock is closed; the flame is then raised, and the contents of the flask are kept boiling gently, until about half the liquid in the flask (a) has distilled over. Some acid must now remain in excess; this is known to be the case if the methyl orange in the absorption-flask does not become yellow.

The two flasks are now disconnected, and if there is any faint smell of ammonia about the distillation-flask (a), the experiment must be started afresh. If all is well, the absorption flask (h), its pipette and the absorption tube are rinsed out with water into a porcelain dish. Excess of chloroplatinic acid solution is added to the contents of the dish: the liquid is then evaporated on a water-bath, and the  $(\text{NH}_4)_2\text{PtCl}_6$  is determined in the same way as the corresponding potassium salt (p. 80). Dry at  $130^\circ \text{C}$ .

*Note.* Instead of distilling from sodium hydroxide, it is perhaps better to distil from slaked lime, particularly when the ammonia is to be determined volumetrically. The concentration of alkali in the solution in the distillation

tion by the stronger alkali.

The determination may be controlled by igniting the precipitate to redness, and weighing the metallic platinum which remains.

For this purpose the crucible containing the double salt is covered and heated very gently for a time. Care must be used, because the ammonium chloroplatinate decrepitates when heated rapidly. The lid is then removed and the heat is gradually increased. The contents of the crucible are finally heated to bright redness, and the residue of metallic platinum is weighed. This residue need not be washed, because  $\text{NH}_4\text{Cl}$  is volatile and cannot remain after ignition.

### Determination of $\text{NO}_3$ in a Nitrate

Many methods are available for the determination of nitrates, volumetric, pp. 133 and 151; gasometric, p. 479; and colorimetric, p. 245. Two gravimetric methods are described below.

The Nitrate is reduced by Devarda's Alloy to Ammonia, which is weighed as  $(\text{NH}_4)_2\text{PtCl}_6$ .

Weigh out accurately about 0.25 gram. of pure  $\text{KNO}_3$  and dissolve it in 30 ml. of water in the flask (a) of the apparatus shown in Fig. 61, p. 83. Then add 3 or 4 gram. of crushed Devarda's alloy (Al 45, Cu 50, Zn 5). The alloy should not be crushed too fine, and dust should be removed or the subsequent reaction may be very violent. The apparatus is set up and dilute hydrochloric acid is placed in the flask (h), as described on p. 83. Place in the funnel (b) some 50 ml. of a concentrated solution of sodium hydroxide, made by dissolving the solid in twice its weight of water. Run half the alkali into the nitrate solution, and heat gently. If the action becomes brisk, remove the flame, and, if necessary, retard the reaction by surrounding the flask with cold water. When the reaction is under control, add the remaining sodium hydroxide.

Now heat the contents of the flask for half an hour, but make no attempt to distil any of the liquid. During this period the nitrate is being reduced to ammonia. After half an hour, gently boil and slowly distil over half the liquid, taking at least a further half an hour for the distillation. If the ammonia is to be determined volumetrically (p. 133), it is most important that none of the very concentrated sodium hydroxide solution finds its way into the hydrochloric acid; the remainder of the procedure is described on p. 84.

When very accurate results are required, it is advisable to carry out a blank, with no potassium nitrate present, in exact parallel with the assay. As many samples of sodium hydroxide contain traces of nitrates, it is advisable to treat the original concentrated solution of the alkali with a small quantity of the crushed Devarda's alloy. The solution is slowly boiled, and the traces of ammonia produced by the reduction of the nitrates are removed by distillation. The solution is then put aside in a stoppered bottle for subsequent use.

**Precipitation with 1:4-Diphenyl-3:5-endanilo-4:5-dihydro-1:2:4-triazole (Nitron).** To the solution to be analysed (which should contain about 1 gram. of nitrate in a volume of 100 ml.) add a little acetic acid, raise almost to boiling and stir in 10 ml. of a 10 per cent. solution of the reagent in N. acetic acid. Then cool the mixture in ice-water for three hours, filter it on a tared sintered glass crucible, and wash the residue with a little cold, saturated solution of nitron in water, sucking the liquid out of the crucible well after each wash. Dry the precipitate at  $105^\circ$  to  $110^\circ \text{C}$ . and weigh it. It has the formula  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HNO}_2$ , and contains 16.53 per cent. of  $\text{NO}_3$ .

*Note.* . . . . . with hydrazine  
sulphate 1 . . . . . be precipitated  
by nitron . . . . . potassium iodate,  
and with . . . . . respectively. Caution is necessary only if present in  
large quantities, and a correction for their presence may be established by making  
a blank determination on a known quantity of a nitrate, to which an appropriate  
quantity of chloride has been added.

### Determination of Carbon Dioxide in a Carbonate

The first method described below is trustworthy; the carbon dioxide is liberated, and is then absorbed and weighed directly.

The second method (p. 89) depends on finding the loss of weight which

the carbonate undergoes by the removal of its carbon dioxide. It may yield somewhat high results.

**Direct Weighing.** The Carbon Dioxide gas is liberated by treating the Carbonate with an Acid; the gas is then absorbed by means of Soda-lime, and is weighed.

The General Description of the Process will be understood by referring to Fig. 62.

The carefully weighed carbonate is introduced into the flask (a), and is decomposed by acid from a pipette, or, preferably, from a dropping-funnel (b). The carbon dioxide which is evolved passes through concentrated sulphuric acid in the glass-bulb apparatus (d), and then

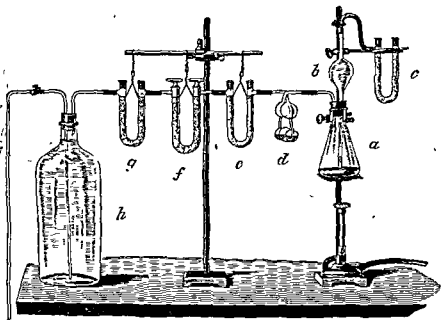


FIG. 62. DETERMINATION OF  $\text{CO}_2$  IN A CARBONATE.

through the tube (e), in which it is freed by anhydrous copper sulphate from any hydrogen chloride which may be in the gas stream. The carbon dioxide is absorbed by the soda-lime contained in the weighed tube (f).

The tube (g) contains calcium chloride, and is intended to prevent water vapour from passing back from the aspirator to the tube (f). The aspirator bottle (h) is used to draw air through the whole apparatus at the end of the process, so as to carry over all the carbon dioxide into the absorption tube (f); this air is freed from carbon dioxide by passing through the soda-lime tube (c) on its way to the funnel (b) and the flask (a). The tube (f) is weighed at the end of the process, and the increase in its weight gives the weight of carbon dioxide which has been evolved from the known weight of carbonate.

**Detailed Description of the Apparatus.** The apparatus consists of a 250-ml. conical flask (a), which is fitted with a rubber bung bored with two holes. Through one of the holes passes a dropping-funnel (b, Fig. 61, p. 83), or a 50-ml. pipette (Fig. 62, b), the lower end of which is drawn out

to a fine point. The bulb of the pipette is filled with the dilute acid, which later on is to decompose the carbonate, and its lower end is just above the bottom of the flask. This is an important point, because any  $\text{CO}_2$  in solution in the acid in (a) is removed fairly quickly if air is drawn through the liquid. Such an arrangement also prevents escape of gas through the pipette.

The upper end of (b) is connected by a piece of rubber tubing to a soda-lime tube (c). If (b) is not fitted with a stop-cock, a screw clamp on this rubber tube is used to control the rate at which air is drawn through the apparatus. The soda-lime in the tube (c) frees this air from carbon dioxide. A piece of bent glass tube is pushed just through the second hole of the rubber stopper in the flask (a), the lower end of the tube being cut off obliquely (see Fig. 61, p. 83). Attached to this tube is a train of bulbs and U-tubes as follows:

The bulb-tube (d) contains concentrated sulphuric acid: this dries the gas, and also acts as a gauge to indicate the rate at which the gas is passing over from the flask (a). Liebig's or Geissler's potash-bulbs serve well for this purpose. The sulphuric acid should half fill the three lower bulbs.

The U-tube (e) has the limb farthest from the bulb-tube (d) filled with granular-tube calcium chloride (see p. 88). The other limb of this U-tube is filled with dehydrated copper sulphate-pumice (p. 88) which absorbs any  $\text{HCl}$  which may be given off during the heating of the liquid in the flask (a).

The stoppered U-tube (f), which is the absorption tube for the  $\text{CO}_2$ , has the limb nearest to the copper sulphate tube (e), the bend, and half the other limb filled with soda-lime, or with soda-asbestos; the remainder of the tube is filled with solid calcium chloride. The soda-lime in this tube becomes hot when it absorbs  $\text{CO}_2$ ; any moisture which is then expelled is absorbed by the calcium chloride, and loss of moisture from the tube is prevented.

Instead of soda-lime or soda-asbestos, a set of Geissler bulbs containing 50 per cent. KOH can be used for collecting the  $\text{CO}_2$ . An additional  $\text{CaCl}_2$  tube should then be introduced next to these bulbs on the side nearest the aspirator. This tube will then retain any water removed from the potash. It should be weighed with the Geissler bulbs.

The tube (g) is filled with granular chloride. Its purpose is to prevent water vapour diffusing back from the aspirator (h) to the weighed tube (f). The tube (g) is not weighed, and it is not connected to the aspirator until the evolution of  $\text{CO}_2$  has ceased and it becomes necessary to draw air through the apparatus.

The Winchester bottle shown in Fig. 62 can be replaced by a wash-bottle. A length of rubber tubing fitted with a clip is attached to the glass tube of the bottle through which it is customary to blow. The other tube, the usual outlet tube, is attached to the last  $\text{CaCl}_2$  tube (g). A stream of air may be started through the apparatus by sucking gently at the end of the rubber tube.

**Preparation of the Absorption Tubes.** A convenient form of U-tube for containing solid absorbents is shown in Fig. 63. This tube is thoroughly cleaned, rinsed with distilled water and dried. As the absorbent must always be protected from the air, the vertical limbs are closed with rubber bungs or with waxed



in the glass tube, and then close (b) with the stop-cock or screw clamp. If the level of the water in the tube remains constant for two minutes, the apparatus is air-tight. Any leak must be discovered and stopped, probably by the replacement of a faulty piece of rubber tubing.

**Procedure.** The absorption tube (f) is first wiped clean and dry, carefully weighed and placed in the train. About 1 gm. of precipitated calcium carbonate, or of Iceland spar, accurately weighed, is placed in the flask (a). Then approximately 30 ml. of hydrochloric acid, made by diluting the concentrated acid with three times its volume of water, are put into the dropping-funnel or pipette. The bung carrying (b) is then put into the neck of the flask and is bound down, if necessary, by thin wire. The aspirator (h) is not attached until later.

The clamp above the pipette, or the stop-cock of the dropping-tube, is now slightly opened, and the acid is allowed to drop slowly upon the calcium carbonate in the flask. Carbon dioxide will be evolved, and will drive the air out of the flask. The bubbles should pass through the sulphuric acid at such a speed that they can be counted easily.

When no further effervescence occurs, the aspirator is attached, the clamp above the pipette (or the stop-cock) is opened, and a slow stream of air is drawn through the apparatus. At the same time the flask is heated gently until the liquid in it just does not boil. The carbon dioxide in solution is then expelled. The current of air displaces the  $\text{CO}_2$  from the flask, the bulbs, and the first U-tube, and carries it into the absorption tube (f). The speed of the air current is so regulated that the bubbles can be counted as they pass through the bulb-tube (d).

In order to make sure that the whole of the carbon dioxide has been collected, a volume of air, equal to about six times the capacity of the apparatus, should be drawn through it. The U-tube (f) is then disconnected. The stoppers are at once turned so as to close the side-tubes; or, if an ordinary U-tube has been used, the rubber caps are slipped over the side-tubes. The tube is allowed to cool to the temperature of the room (allow half an hour) and is then weighed. In very accurate work the U-tube should be kept in the balance-case before the final weighing and also before the initial weighing, so that the two are made under exactly the same conditions. Also it should be weighed against a counterpoise tube of the same size and shape and containing approximately the same quantity of the materials. The increase in weight is the weight of  $\text{CO}_2$  originally present in the calcium carbonate taken.

**Determination of Carbon Dioxide by Difference.** The Carbon Dioxide gas is driven off by treating the Carbonate with an Acid, and the loss of weight gives the amount of Carbon Dioxide in the Carbonate.

It is a general principle of quantitative analysis that when a compound is driven off during an assay, it is much more accurate to collect and weigh that compound than to find its weight by difference by weighing the original vessel before and after the experiment. The first method for determining  $\text{CO}_2$  is therefore more accurate than that now to be described. When the difference method is used it is difficult to be certain that all the  $\text{CO}_2$  has been driven off and that nothing other than  $\text{CO}_2$  (such as water vapour) has been lost.



The carbonate is sometimes decomposed by dilute  $\text{HCl}$  or  $\text{HNO}_3$ , but the method is better suited for the determination of carbonates which can be completely decomposed by  $\text{H}_2\text{SO}_4$ . As heat must be used to drive out  $\text{CO}_2$  from solution, almost necessarily a certain amount of a more volatile acid will be lost and the results will be too high. Hydrochloric acid, however, can be trapped in a tube containing copper sulphate-pumice.

The apparatus described below can only be used successfully after much practice on a standard carbonate. The optimum conditions must be found and these conditions must be adhered to rigidly.

**A Modified Form of the Schrötter Apparatus** is shown in Fig. 64. It should be made of thin glass, and its total weight should be less than 50 grm. It consists of a dish, with a ground-glass lid, in which the carbonate is placed. Passing through the lid of the dish are a reservoir (provided with a stopper and tap) and a gas-washer.

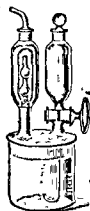


FIG. 64. MODIFIED  
SCHRÖTTER  
APPARATUS.

The reservoir is filled with dilute acid. By removing the stopper of the reservoir and opening the stop-cock this acid is introduced into the flask, where it reacts with the carbonate. The liberated carbon dioxide passes up through the inner tube of the washer, which is half filled with concentrated sulphuric acid. The gas passes down again and escapes through two holes at the bottom of the inner tube.

The percentage of  $\text{CO}_2$  in sodium carbonate can be determined by this method. The salt is conveniently prepared in a pure state by heating pure sodium bicarbonate to dull redness in a platinum crucible. Weigh out accurately about 1 grm. of the prepared carbonate and place it in the dish. Fill the reservoir with cold, 20 per cent. sulphuric acid. Then weigh the whole apparatus as accurately as possible. Run the dilute acid slowly upon the carbonate. Bubbles will at once pass through the washer. Their speed must be so regulated that they can be counted easily, or otherwise the gas will not be dried completely.

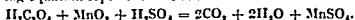
When all the dilute acid has been run into the flask and bubbles of gas no longer escape freely, the apparatus is placed on a closed water-bath. At the same time an aspirator (p. 80), is attached to the outlet of the washer and a slow stream of air is drawn through the apparatus. The volume of air used should be about ten times that of the flask, and it is advisable to interpose a calcium chloride drying-tube between the apparatus and the wash-bottle. Then allow the flask to cool to the temperature of the room, and weigh it under exactly the same conditions as before. When standing prior to weighing, the apparatus must be kept closed, but, if a rubber cap is used, this must be removed before the actual process of weighing. The loss in weight is the weight of the carbon dioxide.

As very few carbonates are quantitatively decomposed by dilute sulphuric acid, hydrochloric acid must often be used in its place. Some of this acid will be carried over by the stream of carbon dioxide, and a tube containing pumice impregnated with anhydrous  $\text{CuSO}_4$  (p. 88) should be attached to the end of the washer and weighed with the apparatus.

Determination of  $C_2O_4$  in an Oxalate

The Oxalate is mixed with Manganese Dioxide, and the mixture is heated with Sulphuric Acid. The weight of the  $CO_2$  evolved is found by absorption in Soda-lime. The weight of the  $CO_2$  evolved is equal to that of  $C_2O_4$  in the oxalate.

The following equation represents the reaction :



The same apparatus is used as for the determination of carbon dioxide in a carbonate by the absorption method.

Weigh out accurately about 0.6 gm. of finely-powdered, pure potassium tetroxalate,  $KHC_2O_4.H_2C_2O_4.2H_2O$ , and mix it intimately with about three times its weight of finely-powdered manganese dioxide, which must be free from carbonate. (See *Note*.) Introduce this mixture into the decomposition flask. Add to it dilute sulphuric acid, and proceed as described on p. 189; start the decomposition by heat.

*Note.* If any carbonate is present in the manganese dioxide, the finely-powdered dioxide should be heated for about fifteen minutes with a small quantity of very dilute sulphuric acid. The oxide is then washed free from acid, and dried.

A Volumetric Method for the determination of an oxalate is given on p. 157, and another Gravimetric Method is described on p. 71.

## Determination of Water, present in the Free or Combined State

Of the four methods described below the first and second apply to substances which lose all their water, but undergo no further change in composition, when they are heated. The water may be determined in such cases by the loss of weight which the substance undergoes.

The third method is generally applicable, but it is used necessarily for substances which, when they are heated, not only lose their water, but also undergo further chemical change involving alteration in weight. Many pure compounds and the great majority of ores, minerals, coals, etc., belong to this class. Examples are ferrous sulphide and ferrous carbonate, which increase in weight by oxidation when they are heated in the air; the latter also undergoes change of weight by loss of  $CO_2$ . The water evolved when such substances are heated must be collected and weighed. The difference method is useless.

The fourth method applies to the determination of water in those substances, such as certain minerals, which lose only water and carbon dioxide when they are heated. A volumetric method is described on p. 106.

The Substance is dried by Heating it in a Steam-oven or other suitable apparatus, and the loss of weight is found.

This method is applicable to substances which lose their moisture, without undergoing further chemical change, when they are heated moderately.

Weigh out accurately about 1.5 gm. of crystallised oxalic acid,  $H_2C_2O_4.2H_2O$ , between a weighed pair of watch-glasses with clip (Fig. 7, p. 11). Then remove the upper glass and clip, and heat the lower glass containing the substance for two hours in steam-oven. Replace the upper glass and the clip, and weigh the glasses with their contents, after they have cooled in a desiccator. Repeat the above process of heating, cooling and weighing, until two successive weighings give the same result.

The water which can be expelled at  $100^{\circ}\text{C}$ . is then known to have been completely removed, and its percentage can be calculated from the difference in weight.

The Substance is dried by Igniting it, and the loss of weight is determined by Difference.

This method is applied to substances which lose all their water without undergoing further chemical change, when they are heated at a high temperature. It is generally to be preferred to any other, if the nature of the substance to be dried permits, since it is carried out with ease and rapidity.

Weigh out accurately about 15 gm. of finely-powdered, pure, recrystallised barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , into a platinum crucible of known weight. Heat the covered crucible gradually over a small Bunsen flame, slowly raising the temperature until the bottom of the crucible is at a dull red heat. Remove the lid and keep the crucible at this temperature for at least fifteen minutes; then allow it to cool in a desiccator, and weigh it. Repeat the above processes, heating for five minutes only, until two consecutive weighings give identical results. The water has then been expelled.

The Substance is heated to a suitable temperature and the Water Vapour is conveyed by a stream of air into an Absorbent Substance and weighed.

This method applies to substances which lose their water when they are heated, and which also undergo a change in weight during the process owing to some other chemical change.

*Description of the Apparatus.* A hard glass tube, about 1 cm. in bore and 15 cm. in length, has a bulb about 4 cm. in diameter blown in its middle (Fig. 65, a). The sharp edges of the ends of this tube are rounded off in the blowpipe flame. Two U-tubes are filled nearly to the level of

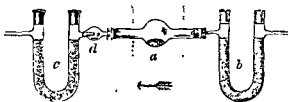


FIG. 65. DETERMINATION OF WATER.

their side-tubes with granular calcium chloride; glass-wool plugs are then pushed into each limb, and the open ends are finally closed with sound corks, which are cut off level with the glass, and are then brushed over with molten paraffin wax. A full description of the filling of the U-tubes and of the preparation of the calcium chloride will be found on p. 88. If carbon dioxide is evolved when the substance is heated, it is important to ensure that the calcium chloride is free from calcium oxide. The U-tubes are then fitted to the bulb-tube (a) by rubber bungs. To the arm side of the tube (c) farthest from the bulb is attached a small bubbler (not shown) containing concentrated sulphuric acid, to indicate the speed at which air is passing through the apparatus. An aspirator (p. 86) is attached to the far end of the bubbler.

When the bulb is to be heated at a high temperature, discs of metal or of asbestos millboard should be slipped over the bulb-tube in the positions shown by the dotted lines in the figure, to prevent the rubber bungs from being scorched. After the separate parts have been fitted together, the whole apparatus must be tested to ascertain if it is air-tight (see p. 88).

*Procedure.* The U-tube (c) is detached and is accurately weighed. The perfectly clean bulb-tube (a) is dried, preferably by drawing a current of air through it while it is being heated, and then cooled and weighed.

About 2 grm. of the finely-powdered substance, such as  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , are placed near the end of a little trough of stiff glazed paper, which will slip easily into the bulb-tube. This paper is pushed into the tube until the powder is within the bulb, and, by rotating the bulb-tube or the trough on a horizontal axis, the whole of the powder is transferred to the bulb. The paper trough is then removed, and the bulb is weighed again. The gain in weight is the weight of salt taken. The apparatus is then fitted together as before, and tested again to see that it is air-tight.

A slow stream of air is then drawn through the apparatus, at such a rate that separate bubbles can be counted in the bubbler. The air is dried by the calcium chloride in the tube (b) before it passes into (a). It then carries the water vapour, which is expelled from the substance by heat, into the bulb (d) and the calcium chloride of the weighed U-tube (c). The sulphuric acid in the bubbler protects the weighed U-tube from moisture which might diffuse backwards from the aspirator.

The temperature of the bulb is slowly raised by a small Bunsen flame until it reaches dull redness, and the salt is heated in the air current until no small drops of water remain on the cool part of the tube (a). The weighed U-tube (c) is then detached, closed, allowed to cool for half an hour, and reweighed. At the end of the experiment the water is shaken out of the bulb (d).

The determination of water in almost any substance can be carried out by this method or by some modification of it. Thus, though many sulphates on heating easily lose  $\text{SO}_3$ , which would interfere, the  $\text{SO}_3$  can be fixed by mixing pure sodium pyrosulphate with the original substance. Some minerals lose silicon tetrafluoride, which again would interfere. This can be kept back by mixing pure lead oxide with the powdered rock.

When the water is to be expelled from the substance at a known temperature, it is necessary to have the bulb-tube (a) either surrounded with an air-bath made of asbestos cardboard, or bent in such a way that the bulb can be immersed in a hot liquid. The air-bath or liquid is heated to the required temperature, which is measured by a thermometer. Tubes specially shaped for immersion in the liquid may be made or purchased.

In laboratories where a convenient supply of electric power is available, the following apparatus can profitably replace the bulb-tube (a): A piece of Vitreosil or hard glass tube about 6 inches long and 1 inch in diameter is wound with Nichrome ribbon, which, in turn, is covered with asbestos webbing. On passing an electric current through the ribbon, the tube is heated. It is, in fact, a small electric tube-furnace. Care should be taken to wind the ribbon in such a way that as much as possible of the tube is heated, but that there is no risk of burning the rubber bungs at the ends.

It is customary to determine the water contents of coals and certain ores by heating them at some standard temperature, generally  $105^\circ \text{C.}$  that is, slightly higher than the boiling-point of water. Such a temperature can be obtained and maintained quite easily by electric heating if an ammeter and a variable resistance are in the circuit. The temperature can be measured by a

the drying-tube (b)  
 thermometer must be  
 determined is weighed,  
 the end (d) to the

Some substances, certain types of coal for example, react with air at 105° C.

**Brush and Penfield's Method for the Determination of Water.** The mineral or other compound is heated in a bulb-tube of suitable material and the water evolved is collected in another part of the tube and weighed. Before choosing a tube it is best to carry out some preliminary experiments possibly by heating the substance in air to constant weight, to determine the minimum temperature required. The choice of material for the bulb-tube—Pyrex, hard glass, or fused silica—is governed by this temperature.

Take a piece of suitable tubing some 25 cm. in length and about 0.6 cm. internal diameter and blow a small bulb on the end and two bulbs near

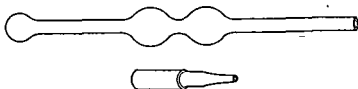


FIG. 66. PENFIELD'S METHOD FOR WATER.

the centre (Fig. 66). The open end of the tube should be partly closed by a piece of capillary tube connected to it by a piece of rubber tubing. This tends to prevent convection currents. Clean the apparatus thoroughly, and dry it by heating it and at the same time drawing a current of air through it. Even if the tube looks dry, this drying in air is probably necessary. Then make a thistle funnel with a long stem which can reach right into the end bulb. This stem must be air-dried on the inside and reasonably dry on the outside.

Weigh the tube. Then weigh out approximately 1 gm. of the substance to be examined and introduce it, *via* the thistle funnel, into the end bulb. Weigh the tube and substance accurately. Clamp the apparatus horizontally and close it with the capillary stopper. Fix an asbestos shield between the bulb end and the nearer of the centre bulbs to prevent these bulbs receiving an excessive amount of heat. Wind round the centre bulbs a lamp wick soaked with cold water, the ends of which should be left dangling in cold water. Then heat the substance to the required temperature for at least fifteen minutes. If the tube shows signs of collapsing it may be turned round gently, or it may be wrapped with platinum foil. Any water evolved will collect in the centre bulbs.

When the action is over, seal a small piece of glass tubing, as a handle, to the hot bulb, and drive away any moisture which may be too near the end by heating carefully. Then collapse the tube in the flame somewhere between the end and the centre and draw off the end bulb and the spent substance. If the substance is allowed to cool before it is sealed off, it

will very probably unite again with some of the water which has been expelled.

After the piece of tube containing the water has cooled, remove the wick and wipe over the glass. Remove the capillary stopper and weigh the tube and the water. Then remove the water by warming the tube gently and at the same time drawing a current of air through it. Allow the tube to cool. Weigh it.

### Determination of Cadmium in its Soluble Compounds

The Cadmium is precipitated as Sulphide,  $\text{CdS}$ , and is converted to Sulphate,  $\text{CdSO}_4$ , and weighed as such.

For practice weigh out accurately about 0.5 gm. of pure recrystallised cadmium iodide,  $\text{CdI}_2$ . Dissolve it in about 250 ml. of water, and add 2 ml. of concentrated  $\text{H}_2\text{SO}_4$  per 100 ml. of solution. Heat the solution to  $80^\circ \text{C}$ ., and pass in hydrogen sulphide until the liquid smells strongly of this gas. After about thirty minutes filter the  $\text{CdS}$  on an ordinary filter-paper, and make certain that all the cadmium has been precipitated, by diluting a portion of the filtrate and passing  $\text{H}_2\text{S}$  through it again. If no further precipitation occurs, wash the precipitate with dilute hydrogen sulphide solution.

Transfer as much as possible of the precipitate to a small, weighed porcelain dish, which should be unglazed on the outside. Remove the residue from the paper by washing with successive small quantities of hot  $\text{HCl}$  diluted with three times its own volume of water. Collect the runnings in the dish and warm until all the precipitate has dissolved and the smell of  $\text{H}_2\text{S}$  has disappeared.

Add a moderate excess of sulphuric acid diluted with its own volume of water. Carefully evaporate to dryness, and then heat to just below red heat, preferably with the small dish in a somewhat larger dish. The residue of cadmium sulphate should be pure white; if it is slightly yellow it has probably been ignited at too high a temperature, and there is some oxide present. In this event, moisten the residue with a small quantity of dilute sulphuric acid and again evaporate to dryness, igniting at a slightly lower temperature.

If, as with cadmium iodide, the cadmium is present in a solution from which all other substances can be expelled by fuming with sulphuric acid, the precipitation with hydrogen sulphide is unnecessary and the sulphuric acid can be added straight away. It is not advisable to collect the cadmium sulphide and weigh it, because the precipitate is not of constant composition. It almost invariably contains double salts of the type  $\text{Cd}_2\text{Cl}_2\text{S}$ .

An Electrolytic Method for the determination of Cd is given on p. 232.

### Determination of Antimony in its Solutions

The Antimony is precipitated as Sulphide,  $\text{Sb}_2\text{S}_3$ , and is weighed either as such, or, if it is present in small quantity, as the oxide,  $\text{Sb}_2\text{O}_3$ .

**Precipitation as Sulphide,  $\text{Sb}_2\text{S}_3$ , and Determination as such.** About 0.5 gm. of anhydrous tartar emetic,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ , is accurately weighed. This is dissolved in about 200 ml. of distilled water in a conical flask, and enough concentrated  $\text{HCl}$  is added to bring the  $\text{HCl}$  content to 20 per

cent. of the whole volume. The flask is then placed in a vessel of boiling water, and a slow stream of  $\text{H}_2\text{S}$  is passed through the hot solution.\* If the temperature is too low, the precipitate will be difficult to handle; if it is too high, antimony will be lost (*Note*). The method described produces a suitable temperature, and the precipitate, yellow at first, finally becomes dark red. The solution is diluted with an equal volume of water, and if the liquid becomes turbid, more  $\text{H}_2\text{S}$  is passed until the liquid is perfectly clear. The precipitate, which will be a mixture of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$ , is collected in a Gooch or alundum crucible, and is washed with water containing a little  $\text{H}_2\text{S}$ . The precipitate is next washed, first with water to remove acid and then with alcohol. Next, air is drawn through the crucible until the precipitate is dry.

The crucible is now placed in a wide glass tube, closed at one end, and about 20 cm. long. The other end of this tube is closed by a rubber bung which carries two tubes, an inlet and outlet tube, for pure, dry, carbon dioxide. The tube and crucible are now heated near  $180^\circ\text{C}$ . in a slow stream of carbon dioxide for half an hour, and then raised at  $280^\circ$  to  $300^\circ\text{C}$ . for two hours. During this time any  $\text{Sb}_2\text{S}_5$  decomposes to  $\text{Sb}_2\text{S}_3$  and the liberated sulphur volatilises. The crucible is then cooled in an atmosphere of carbon dioxide, because the hot sulphide is easily oxidised by the oxygen of the atmosphere, and weighed.

A convenient method for heating the tube containing the crucible is as follows: A piece of sheet asbestos is placed as a false bottom in a deep iron pot, which is to be the heating-oven. A thermometer is bound to the outside of the tube with iron wire in such a way that the bulb is as near as possible the crucible. The tube with the thermometer attached to it is pushed through a hole in a second, somewhat larger, piece of asbestos. This fit should be good. The bottom of the tube is then rested on the false bottom of the pot, and the second piece of asbestos is pushed down the tube to form a lid to the pot. The tube should be so slanted that it is about  $30^\circ$  from the vertical. The iron pot is heated on a ring burner.

An electric tube-furnace large enough to contain the wide glass tube is ideal for drying the precipitate.

*Note.* Both antimony pentachloride and antimony trichloride are extremely volatile compounds. The loss of antimony at temperatures so low as  $110^\circ\text{C}$ . is quite appreciable, and much metal can be lost by evaporating a solution in concentrated  $\text{HCl}$  to dryness. These facts must be remembered when experiments with antimony are being carried out.

**Precipitation as Sulphide,  $\text{Sb}_2\text{S}_3$ , followed by conversion into Oxide,  $\text{Sb}_2\text{O}_3$ , and Determination as such.** The antimony compound is precipitated as sulphide, as described. The sulphide is collected in a filter-paper and washed with  $\text{H}_2\text{S}$ -water and dried at  $100^\circ\text{C}$ . As much as possible of the precipitate is transferred to a small, weighed dish, of 30 ml. capacity, unglazed on the outside. Wet the residue on the paper and transfer it to the dish, by washing it through with successive small quantities of boiling ammonium sulphide solution which must have been freshly-prepared by saturating dilute ammonia with  $\text{H}_2\text{S}$ . Evaporate carefully to dryness.

The sulphide is converted to oxide as follows: Place the dish

containing the antimony and a similar dish containing fuming nitric acid (sp. gr. 1.5) side by side on a sheet of glass, cover them with a bell-jar, and leave them overnight. In this way much of the sulphide is quietly oxidised and any violent reaction is avoided. Then add concentrated nitric acid to the residue and evaporate nearly to dryness on a water-bath. Add a little water, and then ammonia until the solution is alkaline, and evaporate to dryness. The residue should be white.

Ignite the precipitate slowly until the sulphuric acid, produced by the oxidation of the sulphur, is expelled. Finally heat it at  $800^{\circ}\text{C.}$ , at dull red heat for half an hour. This final heating can conveniently be carried out in a muffle furnace in an oxidising atmosphere, but it is most important that no partly-burnt gas comes in contact with the oxide. The  $\text{Sb}_2\text{O}_4$  is very easily reduced to  $\text{Sb}_2\text{O}_3$ , which is volatile, and antimony will be lost.

**Volumetric Methods** for the determination of antimony are given on pp. 168, 182 and 283.

### Determination of Arsenic in Solutions containing this Element in the Arsenious Condition

The Arsenic is precipitated as Arsenious Sulphide,  $\text{As}_2\text{S}_3$ , and is weighed as such.

Weigh out accurately about 0.5 gm. of pure resublimed arsenious oxide. Place the substance in a 500-ml. flask, and add about 50 ml. of dilute hydrochloric acid. Heat the flask on a water-bath until all the solid is dissolved, care being taken that the temperature of the solution does not reach  $100^{\circ}\text{C.}$  If this temperature is exceeded, some of the arsenic will be volatilised as chloride.

If any  $\text{As}_2\text{O}_5$  is present, add a few drops of sulphurous acid solution to convert the  $\text{As}_2\text{O}_5$  into  $\text{As}_2\text{O}_3$ , and then heat the flask on a water-bath until all smell of  $\text{SO}_2$  has disappeared.

Cool the liquid, and dilute it considerably with concentrated  $\text{HCl}$  diluted with its own volume of water. Precipitate the arsenic as  $\text{As}_2\text{S}_3$  by passing hydrogen sulphide gas through the cold solution.

After the covered beaker has stood for an hour, collect the precipitate in a filter-crucible. Wash it with a solution of hydrochloric acid diluted with its own volume of water, which has been saturated with  $\text{H}_2\text{S}$ . Next wash it with alcohol and then with carbon disulphide to remove any free sulphur. Dry the precipitate at  $105^{\circ}\text{C.}$  to constant weight.

**Another Gravimetric Method** for the determination of arsenic is given on p. 79, volumetric methods on pp. 166, 182 and 258, and a colorimetric method on p. 248.

### Determination of Tin in a Stannous or Stannic Compound

The Tin is obtained in solution in the Stannic form and is converted to the Dioxide,  $\text{SnO}_2$ , by hydrolysis.

If no salt or alloy containing a known percentage of tin is available, it is best as an exercise to start with pure, metallic tin. Weigh out about



0.3 gm. of the metal and dissolve it in a 500-ml. beaker in 20 ml. of dilute hydrochloric acid. In order to convert the stannous chloride so produced to stannic chloride, add 5 ml. of hydrogen peroxide to the solution and warm. It must be remembered that chloride solutions containing tin must not be boiled because  $\text{SnCl}_4$  is volatile in steam.

Dilute to 300 ml. and titrate with a dilute solution of ammonia, using methyl orange as indicator, until the solution is neutral. Then add 20 gm. of  $\text{NH}_4\text{NO}_3$  as a concentrated solution. Heat the contents of the beaker just below boiling for fifteen minutes, and then leave in a warm place until the precipitate has settled and the solution is clear.

Collect the precipitate on an ordinary filter-paper, washing it with hot water to which a little nitric acid and ammonium nitrate have been added, until the filtrate is free from chlorides. Dry the precipitate and filter-paper and burn the paper apart from the precipitate. Use a porcelain crucible, because there is some danger of the  $\text{SnO}_2$  being reduced to tin, which would alloy with a platinum crucible. Moisten the cold residue with 2 drops of concentrated nitric acid. Cover the crucible, and heat it carefully to expel the excess of acid. Then raise the temperature to a red heat for a short time. Cool. Repeat the treatment with acid, heat strongly for a short time, cool and weigh.

Care must always be used when damp  $\text{SnO}_2$  is being heated, because the dioxide spatters very easily. As it is also easily reduced to the metal, it must always be shielded from unburnt gas and heated in an oxidising atmosphere.

Volumetric Methods for the determination of tin are given on pp. 165 and 182, and are usually to be preferred to the gravimetric method.

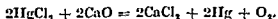
### Determination of Mercury in its Compounds

Three methods are given. In the first, the mercury is separated, and weighed as metal. A modification of this method is described on p. 260; the mercury is separated from its sulphide ore by heating the ore with iron filings, then allowed to amalgamate a sheet of silver, and weighed with the silver.

In the second method the mercury is precipitated and weighed as sulphide. This is useful for solutions of mercuric compounds, and for the separation of mercury from metals which are not precipitated by hydrogen sulphide. It gives excellent results, but if nitric acid is present, it is best to use the third method, because any attempt to remove nitric acid by evaporation in the usual way results in the loss of a considerable proportion of the mercury.

In the third method the mercury is precipitated from a solution of the mercurous salt as  $\text{Hg}_2\text{Cl}_2$ , and is weighed as such.

The Mercury Compound is decomposed by heating it with Calcium Oxide, and the escaping Mercury vapour is condensed, and is weighed as Metal.



The reduction is carried out in the apparatus shown in Fig. 67. A piece of combustion tube, about 1 cm. in internal diameter and about 50 cm. in length, is closed by drawing it off at one end (a) in the blowpipe. Powdered

magnesite is introduced into the clean, dry tube to form a layer 5 cm. in length (*a-b*).

About 1 gram. of pure mercuric chloride is then weighed accurately, and is mixed intimately with powdered quicklime in a porcelain mortar (*Note 1*). This mixture is introduced into the tube (*b-c*), and the mortar is

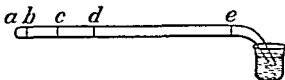


FIG. 67. DETERMINATION OF MERCURY.

riused out with a little more quicklime, which is also transferred to the tube (*c-d*). The tube is then filled with powdered quicklime to within 5 cm. of its open end, the powder being kept in its place by pushing in a loose plug of asbestos at (*e*).

The open end of the tube is now drawn out in the blowpipe flame and bent obliquely as shown in the figure. A passage along the whole length of the tube is formed by holding the tube horizontally and tapping it gently upon the bench. The tube is then laid in a combustion furnace (p. 428) on an iron trough covered with asbestos, so that the end of the bent tube dips just beneath the surface of water in a small weighed beaker.

The front portion of the tube (*c-d*) is now gradually heated to redness. The heat is then slowly extended to that part of the tube which contains the mercury compound, and this is heated until the whole of the tube from (*e*) to (*b*) is at a bright red heat. In this way the mercury is set free in the form of vapour, which is condensed to liquid as it passes into the water in the beaker. The magnesite in (*a-b*) is finally heated to redness so as to produce a stream of carbon dioxide gas, which sweeps out the last traces of mercury vapour from the tube into the water.

While the tube is still red hot, the narrow delivery tube is cut off at the bend by means of a cold file, and any mercury which has condensed in this portion of the tube is washed out and added to the main portion in the beaker (*Note 2*). The globules of metal are now united into one mass by gently agitating the contents of the beaker. The water is poured off as far as possible, and the rest is removed by absorbing it with filter-paper. The mercury is dried finally over concentrated sulphuric acid in a desiccator to constant weight. The percentage of mercury present in the original substance may be calculated from the weight of mercury found.

This method gives results which are somewhat too low. The method of collecting the mercury on silver foil, described on p. 260, is to be preferred to the collection under water, but wherever possible the mercury should be precipitated and weighed as  $\text{HgS}$ , as described below.

*Note 1.* Mercuric iodide is not decomposed by heating with lime; powdered copper must be used instead. If the mercury is present as sulphide, a little metallic iron must be mixed with the lime to hasten the reduction.

*Note 2.* The mercury may prove reluctant to leave the tube or to unite into one drop. In this case dissolve it in a small quantity of nitric acid at  $80^{\circ}\text{C}$ . and determine the mercury either gravimetrically as mercurous chloride (see below), or, better, volumetrically by the thioyanate method (p. 199).

The Mercury is precipitated as Sulphide,  $\text{HgS}$ , and is weighed as such.

Weigh out accurately about 0.3 gm. of pure mercuric chloride into a 500-ml. beaker. Dissolve the salt in about 300 ml. of water, add a few drops of dilute hydrochloric acid, and pass hydrogen sulphide into the cold liquid until it is saturated, as shown by the deep black colour of the mercury sulphide precipitate. Allow the liquid to stand until the precipitate has settled, then filter through a filter-crucible. Wash the precipitate with cold water, and weigh it after it has been dried at  $105^{\circ}$  to  $110^{\circ}$  C.

If the precipitate contains free sulphur, it should be washed with alcohol and then with recently-distilled carbon disulphide until the last drops of the washings leave no residue when they are evaporated. The precipitate is then dried as before, after the careful removal of the carbon disulphide in a current of air.

*Note 1.* This method cannot be used when any of the mercury is in the mercurous state (see method below).

*Note 2.* It cannot be used in the presence of nitric acid, which produces high results through the formation of mercuric sulphonitrate  $[\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}]$ .

*Note 3.* If an attempt is made to remove nitric acid by evaporation, mercuric chloride or some other volatile mercury salt will almost inevitably be lost.

*Note 4.* The original solution should contain not more than 0.1 gm. of mercury in 100 ml.

The Mercury is precipitated as  $\text{Hg}_2\text{Cl}_2$ , and is weighed as such.

If the mercury is present in solution entirely as mercurous salt, it may be precipitated directly by the addition of dilute sodium chloride solution. If a mercuric salt is present it must be reduced to the mercurous condition, as is directed below, before precipitating the mercury. This method is suitable even if nitric acid is present.

For practice, weigh out accurately about 0.5 gm. of mercuric chloride, dissolve it in 200 ml. of water and add a small quantity of dilute hydrochloric acid and an excess of phosphorous acid (*Note*). Allow the liquid to stand for twelve hours, then filter through a crucible, wash the precipitate with water, dry it at  $105^{\circ}$  C. and weigh it.

*Note.* The solution of phosphorous acid can be prepared by allowing phosphorus to deliquesce in moist air; or it may be obtained by adding phosphorus trichloride to water, evaporating the solution to dryness to expel the hydrochloric acid and dissolving the residue in water.

### Determination of Silica in a Silicate

The Silica is separated and converted into the insoluble form by adding excess of acid to the Silicate and evaporating to dryness; the Silica is then completely dehydrated and is weighed.

The choice of method depends on whether the silicate can be decomposed by an acid or not. If it is soluble in water, or can be decomposed by strong hydrochloric or nitric acid, it is treated as follows:

For practice, weigh out accurately about 0.5 gm. of finely-powdered "soluble glass," or sodium silicate, into a platinum or porcelain dish. Moisten the powder with water. Place the dish, covered with a clock-

glass, on a water-bath; then gradually run in concentrated HCl diluted with its own volume of water through a small opening made by drawing aside the clock-glass. Stir the contents of the dish continuously. When no gritty particles can be felt with a glass rod, the powder is completely decomposed. Then remove the cover, evaporate the liquid to dryness, and stir the residue continually, breaking up any lumps with a glass rod. When the powder appears to be perfectly dry and no moisture is deposited on a cold clock-glass placed on the dish for a few seconds, add about 10 ml. of dilute HCl and again evaporate to dryness; then treat the residue with 50 ml. of dilute hydrochloric acid and filter through an ordinary filter-paper. Collect all the runnings in a porcelain dish and wash the silica, first with hot, dilute hydrochloric acid and then with hot water, until it is free from chlorides. Retain the precipitate and paper. Evaporate the filtrate, which will contain a considerable percentage of the silica, to dryness, and then heat the dish in an air-oven at  $110^{\circ}\text{C}$ . for an hour. The silica will now be present in the anhydrous and insoluble condition.

As soon as the dish is cold, moisten the powder with hydrochloric acid, and warm the dish on the water-bath for not more than fifteen minutes; otherwise some of the silica will redissolve. Then add hot water, stir well, allow the solid to settle, and decant the liquid through a second filter. Treat the residue thus three times. Then transfer the silica to the filter, and wash it thoroughly with hot water. If the second precipitate of silica is large, the runnings should be evaporated to dryness a second time and the collection repeated.

Now transfer the precipitates to a weighed platinum crucible and ignite the papers wet. At first heat the covered crucible gently, taking care that none of the light, fine silica powder is carried off by the escaping moisture. Increase the temperature gradually until the crucible has reached a bright red heat, and keep it at this temperature for fifteen minutes. Then weigh the crucible, and then repeat the ignition until the weight is constant. Care must be taken during drying and weighing, because the silica will probably be hygroscopic.

*Note.* The silica obtained by the above treatment is almost invariably impure, and should be treated in the following way after it has been weighed:

The ignited silica is heated in a platinum vessel on a water-bath with a pure solution of hydrofluoric acid and a few drops of concentrated  $\text{H}_2\text{SO}_4$ . The hydrofluoric acid should be added down a waxed glass rod. The whole is then evaporated to dryness, and the residue is ignited and weighed. This process is repeated until no further loss in weight occurs. The total loss in weight by the treatment with hydrofluoric acid represents the weight of the silica.

As the laboratory reagents almost invariably contain some silica, it is advisable, in exact analysis, to carry through a blank in parallel with the assay. This is particularly necessary when the silicate is fused with sodium carbonate (see below), and when the silica is determined by volatilisation (see above).

If the silicate is Insoluble in Acids or is not completely decomposed by acids, the silica should be determined by the method given on p. 271.

#### Determination of Fluorine in a Fluoride

The Fluoride is precipitated as Calcium Fluoride,  $\text{CaF}_2$ , and is weighed as such, or as  $\text{CaSO}_4$ .

**Soluble Fluorides.** Neutralise the solution in a beaker with acid or alkali, and then add 2 ml. of a normal solution of sodium carbonate. Heat to boiling

## PART III

# VOLUMETRIC ANALYSIS

*Introductory.* A reaction which is frequently employed in quantitative analysis is that of double decomposition. Suppose, for example, that the chlorine in a solution of sodium chloride is to be determined. The solution is treated with a solution of silver nitrate, and double decomposition takes place :



In gravimetric analysis, advantage is taken of the fact that silver chloride is an insoluble compound. If, therefore, the solution of silver nitrate is added in excess, all the chlorine can be collected and weighed as silver chloride. It follows that the success of a gravimetric analysis normally depends upon the formation, from substances reacting in solution, of an insoluble precipitate. In this way, only, can it be known for certain that the reaction has gone to completion.

If a known weight of silver nitrate (obtained by dissolving a weighed quantity of the salt in a known volume of water and using a known portion of the solution) be added in quantity just sufficient to complete the reaction, then the weight of silver used (and therefore the weight of silver chloride obtained) will also be known without the necessity for collecting, washing and drying the precipitate. It is on this idea that the process of volumetric analysis is based. The end of the reaction may be marked by the fact that the addition of a further few drops of the solution of the precipitant does not cause a precipitate to form ; by a definite change in colour of the reacting mixture ; or by the aid of an "indicator." The indicator may be a third substance, and is generally of such a nature that it will not react with the precipitant until all the substance to be determined has so reacted ; the reaction between indicator and precipitant must be accompanied by an obvious colour change. In the determination of a chloride, which is described in greater detail below, potassium chromate may be used as the indicator. It reacts with silver nitrate to give a red precipitate, but the precipitate forms only when nearly all the chloride has been removed from solution.

The formation of a precipitate, either by double decomposition or with the indicator, is not an essential part of the process. For example, strongly-coloured, soluble compounds are known which are red in the presence of acids and yellow in the presence of bases, and if a mere trace of such a compound is present in a solution of an acid to which a solution of a base is being added, the change in colour will indicate when the base is in the slightest excess. Similarly, if a compound in solution is being oxidised by potassium permanganate, which itself is strongly coloured, but which forms colourless reduction products, the production of a persistent, though very faint, pink tinge in the liquid means that the compound has been completely oxidised and that the permanganate is present in very slight excess.

The fact that the formation of a precipitate is not essential makes

the scope of volumetric analysis much wider than that of gravimetric analysis. It is obvious too that the former is ordinarily much the more rapid, and the belief is current that because it is faster it is also less accurate. This belief is not always justified, because various causes, such as the adsorption of foreign substances on the precipitate and the partial solubility of the precipitate in the mother liquors and in the liquids used for washing, tend to make gravimetric work inaccurate. Each case must be considered on its merits, and there is no general rule to guide the chemist in his choice of method.

*Illustration of a Volumetric Determination.* The determination of chlorine present as chloride in neutral solution, is a typical volumetric method. The chlorine is precipitated as silver chloride by the addition of silver nitrate in solution (see above), in the presence of potassium chromate; any excess of silver nitrate at once produces a permanent brick-red precipitate of silver chromate. The first appearance of a slight but permanent red coloration throughout the liquid accordingly marks the complete precipitation of the chloride.

In a certain determination the solution of silver nitrate which was added contained one-tenth of the molecular weight of silver nitrate, or 16.99 grm. per litre. Hence, according to the above equation, each millilitre of the silver nitrate solution could precipitate 0.003516 grm. of chlorine from the chloride. It was found that 22.5 ml. of this silver nitrate solution were required to react with 2 grm. of the substance dissolved in water. Therefore,

$$\begin{aligned}\text{the weight of chlorine in the substance} &= 22.5 \times 0.003516 \\ &= 0.0798 \text{ grm.},\end{aligned}$$

$$\text{and the percentage weight of chlorine} = \frac{0.0798 \times 100}{2} = 3.99.$$

*Reciprocity of the Method.* It is obvious that the process described above can also be used for the determination of silver. In this case one adds a solution containing a known concentration of the substance, but an unknown concentration of silver, to a solution containing a known weight of sodium chloride. Again the end-point is marked by the first appearance of a permanent brick-red coloration.

In the following pages those processes of volumetric analysis are generally grouped together in which the same liquid reagent or "Standard Solution" is employed. The most important and typical processes in each group are printed in ordinary type, whilst those of less importance are printed in smaller type. Any of them can be carried out on the micro-scale with the apparatus described on p. 114. For additional methods the student should consult the general references on p. 518.

## SECTION V

### CALIBRATION AND USE OF GRADUATED VESSELS STANDARD SOLUTIONS

#### Calibration and Use of Graduated Vessels

*General Considerations.* Refer back to the illustration of a volumetric determination given on p. 105. Suppose that the substance contains 39.9 per cent. of chlorine instead of 3.99 per cent. It would then be desirable to weigh out 2 gm. of the substance as before, to dissolve it in water, and to make up the solution to 250 ml. in a graduated flask, to take one-tenth (namely, 25 ml.) in a pipette and to titrate this tenth against the standard nitrate.

In order to obtain an accurate result it is necessary that :

(a) The pipette delivers exactly one-tenth of the solution from the flask (known as an aliquot portion) ;

(b) The burette delivers  $\frac{22.5}{1000}$  of the weight of silver nitrate in a nominal 1 litre of the solution of silver nitrate.

These conditions *must* be fulfilled. It will be noticed, however, that the true volumes of the solutions used are of no importance provided the fractions are exactly correct. Thus, in the above example it is a matter of indifference whether or not the 250-ml. graduated flask contains 250 or 252 ml., provided that the pipette used delivers one-tenth of the contents, namely, 25.0 or 25.2 ml., respectively.

From these and similar considerations it can be shown that it is nearly always the volume of one vessel relative to another which is important—not the volume of the vessel in absolute millilitres.

*Units.* It is desirable that flasks of the same nominal capacity should have the same real capacity, and it is for this reason that a unit of capacity is necessary. The litre is defined as the volume occupied by that quantity of pure water at 4° C. which has a mass of 1 standard kilogram. One-thousandth part of a litre may be used as the unit of capacity and this volume is correctly written "ml." A cubic centimetre, on the other hand, is the volume of a cube, the length of a side of which is 1 cm. A cubic centimetre of pure water at 4° C. does not weigh exactly 1 gm. (see p. 514). Thus :

1 ml.  $\approx$  1.000028 c.c., and 1 litre contains 1000.028 c.c.

*Calibration of Apparatus.* Reference should again be made to the section on p. 514, on units. Volumetric apparatus should always be calibrated at a standard temperature, or the calibrations should be corrected to some standard temperature. The British Standards Institution has laid down that the standard temperature in this country shall be 20° C., but there is still a large supply of glassware calibrated at 15° C., 15.5° C., or 60° F. The standard temperature in America is 20° C. The error introduced by accepting a vessel which is correct at 15° C. as also correct at 20° C. is very small, about 1 : 10,000. This error

is of absolutely no importance in ordinary volumetric work. For the purposes of this book, a 1,000-ml. flask is considered to be graduated correctly when it holds at 20° C. the volume occupied by a kilogram of water at 4° C., the barometer being at 760 mm. and the temperature of the air surrounding the flask 20° C.

The Table given on p. 407 will be useful when measuring-vessels are being calibrated. It gives the weight of water which a correctly-graduated vessel should contain under different conditions. Empirical methods for the calibration of glass vessels are given on p. 108 and the following pages. Further information should be sought in *Treadwell's Analytical Chemistry*. In very exact volumetric analysis, all volumes should be referred to some standard temperature, but it is almost impossible to make the necessary corrections, because the temperature coefficients of cubical expansion of the various solutions are often unknown. If the following procedure is adopted, errors due to faulty calibration of glass vessels become negligible.

Refer back once more to the determination of a chloride by silver nitrate. Suppose that 2 grm. of the chloride have been weighed out, made up to 250 ml., one-tenth taken, and titrated against the silver nitrate, 22.5 ml. of the latter being used. There thus appears to be about 0.08 grm. of chlorine in the aliquot part, or 0.8 grm. of chlorine in the sample. Now 1.32 grm. of NaCl contains about 0.8 grm. of chlorine. Therefore weigh out 1.32 grm. of pure common salt, dissolve it in water, and make up to 250 ml. in a flask similar in all respects to the first, taking care that the two solutions are at exactly the same temperature. Take one-tenth of this standard solution of sodium chloride, using the same pipette as before, and titrate it against the silver nitrate solution, being careful to deliver the nitrate from the same part of the burette as before. Let the reading be 23.1 ml.

Then 23.1 ml. of the  $\text{AgNO}_3$  are equivalent to the chlorine in 0.132 grm. of NaCl, i.e., to  $\frac{0.132 \times 35.46}{58.46}$  grm. of chlorine.

Therefore 22.5 ml. of  $\text{AgNO}_3$  are equivalent to

$$\frac{0.132 \times 35.46 \times 22.5}{58.46 \times 23.1} \text{ grm. of chlorine} = 0.0780 \text{ grm.}$$

Therefore in 0.2 grm. of the chloride is 0.0780 grm. of chlorine, and the percentage of chlorine is 39.0 per cent.

Consideration will show that this method of using the solution in the burette merely as a kind of balance must lead to very accurate results.

### Volumetric Apparatus

Four types of glass-measuring vessels are in general use for volumetric analysis. These are the measuring flask, the pipette, the burette, and the measuring-cylinder.

**Cleaning Glass Apparatus.** Before glass apparatus is calibrated, it must be thoroughly cleaned by filling the vessels with methylated spirits saturated with sodium hydroxide. After an hour, they are then allowed



to drain, washed with water, filled with concentric sulphuric acid which has been saturated with chromic acid, and left overnight.

As it is essential that the tops of burettes and the necks of flasks be clean, the cleaning liquid must fill these vessels to the very top. Pipettes should be filled by attaching a piece of rubber tubing fitted with a clip to the mouthpiece, sucking up the liquid as far as possible, and closing the clip; or a tall measuring-cylinder can be filled with the liquid and the pipettes placed in it.

Glass apparatus, for no apparent reason, sooner or later, and generally sooner, becomes dirty. When not in use flasks should be stoppered, the ends of burettes should be covered with a test-tube, and the jets protected by pieces of rubber tubing. Water will not run evenly down dirty glassware, but will form drops. As soon as these are noticed an attempt to clean the glass with a test-tube brush dipped in quicklime should be made. If this attempt fails, the apparatus should again be filled with sulphuric-chromic acid mixture. Pipettes should be cleaned frequently with this mixture.

### The Measuring-Flask

Measuring-flasks graduated for 1 litre (1,000 ml.), for 0.5 litre (500 ml.), or 0.25 litre (250 ml.), for 200 ml., and for 100 ml., will be found convenient

for general use. The level at which the upper surface of the liquid stands must be in the neck of the flask (Fig. 69), and the neck should be narrow to ensure accurate readings.

Sometimes two marks are etched on the neck of the flask; one is for measuring and the other for delivering the volume which is marked on the flask. When the flask is filled to the lower mark it contains the stated volume; and when it is filled to the upper mark, the stated volume can be poured out or delivered from the flask.

*Calibration of a Flask for Measuring.* The flask is first thoroughly cleaned and dried. Volumetric apparatus must never be heated, as the glass expands on heating, but does not return to its original volume for a long time, months or years.

Therefore the best way to dry a flask quickly is to wash it out once or twice with a small volume of clean alcohol or acetone. As much as possible of the liquid is drained off, and the remainder is evaporated by blowing a stream of air into the vessel. If a set of foot-bellows is used, remember that, as the air is picked up from near the floor and will therefore be dirty, it must be filtered. The best method of filtration is to stuff the delivery tube lightly with cotton wool.

Select one of the flasks, say the 500-ml. flask, and make it your own personal standard of volume. The 25-ml. pipette, for example, should then deliver one-twentieth of the volume of liquid required to fill the flask. Place the flask on the left-hand pan of a fairly large balance, sensitive to 0.1 gm., and weigh it. Fill the flask with air-free, distilled water which has attained the temperature of the room. A good way of preparing air-free water is to place distilled water in a clean filter-bottle. The bottle is



FIG. 69. LITRE FLASK.

stoppered with a rubber bung and placed in a pan of hot water. On connecting up to the filter-pump, the water will soon boil under the reduced pressure. Remove the warm water and leave the distilled water to come to room temperature, with the pump running.

Now place the full flask on the left-hand pan of the balance. On the right-hand pan place a calibrated 500-grm. weight, if a 500-ml. flask is being calibrated, together with the weights equal to the weight of the empty flask. On the left-hand pan place the required small correcting weights (see Table, p. 497). Then, by means of a thin glass tube, add water to or withdraw water from the flask until the balance is in equilibrium. If drops of water form in the neck, the flask is not clean, and should at once be thoroughly cleaned.

If the cleanliness is satisfactory, take the flask off the balance-pan and gum a thin vertical strip of paper on the outside of the neck. Place the flask on a level surface, and, with the eye at the same height as the top of the liquid, make a thin mark on the paper, level with the bottom of the meniscus. Now empty out the water, which can conveniently be used for the calibration of the other vessels, as it will be at room temperature.

Cover the neck of the flask near the mark on the paper with a thin layer of paraffin wax. Fix horizontally in a clamp a glass tube or wooden rod, of such diameter that it will just slip into the neck of the flask. Slip the neck of the flask over this tube and press the end of the tube against the end of the flask in such a way that the flask can be rotated about it without a wobble. Then place the edge of a very sharp knife against the calibration mark on the paper, and rotate the flask in such a way that a clean ring is cut in the wax. Etch this ring by wrapping around it a piece of cotton-wool soaked in solution of hydrofluoric acid. As the etching of glass is not easy, it is a good plan to practise the etching of rings on a piece of glass tubing before operating on the graduated flask. If the flask was graduated originally and the new and the old rings are not coincident, it is best, in order to avoid confusion, to blur out the old ring with hydrofluoric acid.

The flask is now graduated. The calibration should, however, be checked by drying the flask again, weighing it, and weighing again after so filling it with distilled water that the bottom of the meniscus is level with the graduation ring.

*Calibration of a Flask for Delivering.* The flask is filled with distilled water to the graduation on its neck. The water is poured out, and the flask is allowed to drain in an inverted position for a standard time, say fifteen seconds, and with its lip held steadily against the inside surface of a glass beaker in exactly the same way as it will actually be used. The flask is then closed by a glass stopper or rubber bung to prevent loss of water by evaporation, and the flask placed, with its interior still wet, upon a pan of the balance and counterpoised. The subsequent procedure is the same as in the calibration of the flask for measuring.

Care must be taken not to confuse the two marks on the neck of the flask. The top one is for delivering, the bottom one for measuring.

### The Pipette

Pipettes are of two kinds. The first is designed to deliver a constant

volume of liquid; the second to deliver varying small volumes. They are shown in Figs. 70 (a) and (b), respectively.



(a) (b)  
FIG. 70.  
PIPETTES.

Pipettes are nearly always filled by suction, and the liquid is first raised higher than the graduation. When filling the pipette it is important to cant it and the vessel containing the liquid to an angle of nearly  $45^\circ$ , so that the progress of the liquid up the tube can be easily followed. The end of the pipette is then closed by the tip of the first finger, which should have been slightly moistened; the thumb should not be used. The level of the liquid in the pipette is lowered by slightly relaxing the pressure of the finger and by rotating the pipette. Liquid can thus be run out slowly and under perfect control, and the flow stopped when the lower curve of the meniscus just reaches the graduation ring. Not more than an inch or so of the outside of the pipette should have been allowed to have become wet, and any drops of liquid adhering to the outside are removed by touching it with the nail of a finger of the free hand.

If the pipette has only one graduation, the measured volume may be delivered by removing the finger and allowing the pipette to empty itself, but a standard technique for draining the pipette must be adopted. That recommended is to hold the tip against the side of the receiving vessel while the bulk of the liquid is being delivered, and to continue holding it still for a further fifteen seconds to allow it to drain after the rapid flow has ceased. The outlet should be so shaped that a pipette of a given size delivers the bulk of its liquid in a given time. Thus a 50-ml. pipette should deliver in more than twenty-five seconds and in less than forty seconds (plus fifteen seconds for drainage). These times are given in tabular form on p. 498. Note that the pipette must be calibrated using exactly the same procedure as the procedure adopted when it is in use. A pipette should never be drained by blowing through it, as thereby grease from the mouth is deposited in the barrel. This grease causes drops to stick to the glass, and the dirty pipette delivers a varying quantity of liquid which is always less than that delivered by the clean pipette.

If a drop-pipette is being used, the required quantity of liquid can be delivered by relaxing the pressure of the finger and twisting the tube slightly.

**Calibration of the Pipette.** A pipette can be calibrated as follows: A thin vertical strip of paper is gummed along the upper part of the stem of the pipette, so that it covers only half the tube, and a horizontal mark is made on this paper.

The pipette is filled to the mark with boiled, distilled water at room temperature. This water is then delivered, using the standard procedure, into a beaker, which is covered with a watch-glass. The beaker and the

det  
nor  
from the Table (p. 497) Suppose this latter weight to be the smaller.

A second mark is then made on the paper, considerably below the first mark. The pipette is filled to this second mark and the weight of water determined as before. This weight ought now to be too small. From the two weights, the position in which to place the graduation mark can be calculated. Make this mark, and check by weighing the water delivered from the pipette when the latter is filled to it. The pipette should be filled and emptied at least three times, and the mean weight of the water which is required to fill it is determined.

A ring is now etched round the pipette, using hydrofluoric acid. This process has already been described (p. 100). The pipette can be mounted

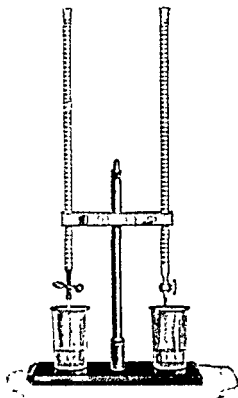


FIG. 71. BURETTES.

FIG. 72.  
MENISCUS.

horizontally for etching, by placing the mouthpiece over a thin glass rod held in a clamp and the other end over a needle forced into a cork.

Micro-Pipettes are usually small pieces of capillary tubing which are calibrated to deliver a desired volume (e.g., 0.1 to 1.0 ml.) for a specified period of drainage; they are therefore easily "home-made."

### The Burette

The Burette (Fig. 71) is a tube of uniform diameter throughout its graduated length. The lower end is considerably narrowed and is closed either by means of a glass tap, or by a pinch-cock which presses upon a rubber tube, or by a glass bead inserted into a narrow rubber tube. In the latter case, liquid is obtained from the burette by gently pressing on the bead and twisting the rubber between the fingers. The

use of any form of burette other than that fitted with a glass tap is to be deprecated, because (a) some of the liquids which will be used will react with the rubber, losing concentration in the process and causing leakage; (b) it is impossible to see whether or not any air has been trapped in the rubber tube. Micro-burettes (see p. 114) are an exception.

A suitable soft grease for lubricating the stop-cock is made by melting together 3 parts of vaselin and 1 part of beeswax. Another suitable grease can be made by warming 3 parts of vaselin and stirring in 1 part of pure rubber in the form of small clippings. Alternatively a wax of the type used in high-vacuum work will serve.

The burette is graduated in millilitres and fractions, and may contain 25, 50 or 100 ml. Those in general use have a capacity of 50 ml., each ml. being divided into tenths. The graduation marks at the ml. units should reach all round the barrel of the burette; at the 0.5-ml. marks, three-quarters; and at the 0.1-ml. marks half-way round.

The burette is filled by closing its lower end and pouring in liquid from the top. The liquid should rise above the highest graduation, and should then be allowed to flow out until the lowest point of the meniscus just touches this graduation (Fig. 72). In Fig. 72 the burette reading is 32.0 ml., not 31.8 ml. However, if the burette is filled with a coloured liquid, such as potassium permanganate, it is more satisfactory to read the top of the meniscus.

In filling the burette, great care must be taken that no air bubbles are left in the tap or jet, because it is assumed that *liquid only* passes out when the burette is in use. The volume of any air bubble which is swept through will be counted as so much liquid, since the volume of liquid which is assumed to have flowed from the burette is measured by the fall of the meniscus. The burette is supported by a convenient clamp and stand (Fig. 71). It should not be held in the hand after it is filled, because an error may be introduced by the expansion of its contents caused by the heat of the hand.

The best way to read a burette is as follows: It is taken out of the stand and held lightly from the top between the finger and thumb, in such a position that the meniscus is on a level with the eye. A white card is then placed behind the meniscus and the reading is taken. The time taken to withdraw and replace the burette is very short, and it is well worth while spending it as the burette comes almost automatically into the correct position and parallax is avoided. A further method of avoiding parallax is to fix on some object at the other side of the room which is at eye level. The burette reading is taken when this mark, the bottom of the meniscus and the eye are in a straight line.

The use of floats or of burettes marked with a blue line behind, or other patent devices to ensure accurate readings is not recommended, except when the saving of a few seconds in a titration is a matter of importance. Liquid should never be run out of the burette at too fast a rate, as then the volume taken appears to be slightly larger than it really is. Suitable times of outflow are given in the table on p. 498. Note that these times depend on the *length*, not on the volume, of the burette.

**Calibration of the Burette.** A burette can be calibrated quickly and accurately with the apparatus shown in Fig. 73. A small, auxiliary

burette, shaped as shown, and of a capacity of about 5 ml., is attached by a thin rubber tube to the end of the apparatus to be calibrated. The connection inside the rubber tube should be glass to glass. Both burettes must be spotlessly clean.

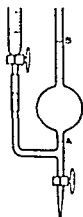


FIG. 73.  
AUXILIARY  
BURETTE.

Distilled water is run through both burettes until every bubble of air has been removed from the narrow glass tubes and from around the cocks. The larger burette is then filled with boiled, distilled water at the temperature of the room, to the 0-ml. graduation, and so that the water stands at the mark A in the auxiliary burette. Then water is run from the large to the small burette until the level is at the 5-ml. mark on the former, and a mark B is made on the latter by sticking a very thin piece of paper round it on level with the meniscus. The water between the two marks is run into a weighing bottle, which is then stoppered and weighed.

The auxiliary burette is filled again to the mark B, the reading of the large burette is taken, and the water is emptied into the beaker, and so on till the 50 ml. have been run out.

The beaker and water are now weighed. If the burette has been correctly graduated in the first place, the successive readings will have been 5.0, 10.0, etc., ml., and the total weight of the water will be the weight of 50 ml. of water under the given conditions. This weight can be found from the Table on p. 407. The experiment should be carried out three times and the mean results taken.

If the error over the whole burette is greater than 0.1 ml., it is advisable to select another. If necessary, a curve can be drawn to express the burette errors.

In a special case the laboratory conditions were such that 49.903 gm. of water were required to fill correctly a glass vessel graduated to hold 50 ml.

The first six burette readings were 0.00, 5.00, 9.95, 14.98, 20.05, and 25.08 ml. The weight of water required to fill the auxiliary burette ten times was 50.005 gm.

Now, as 49.903 gm. is the weight of 50 ml. of water,

$$50.005 \text{ .. .. } \frac{50 \times 50.005}{49.903} = 50.1 \text{ ml.}$$

Hence the capacity of the auxiliary burette is 5.01 ml.

Therefore the volume of the burette between the 0 and 5 graduations is 5.01 ml.; between the 0 and 10 graduations, it is  $[(10 - 9.95) + 5.01 \times 2] = 10.07$

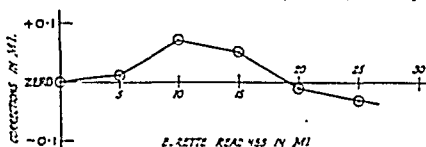


FIG. 74. BURETTE CORRECTION CHART.

ml.; between 0 and 15,  $[(15 - 14.98) + 5.01 \times 3] = 15.05$  ml. At the 20 mark it is 19.97; and at 25 it is 24.97 ml.

Thus +0.01, +0.07, +0.05, -0.01, and -0.03 ml. have to be added

to the nominal volumes to obtain the actual volumes delivered by the burette between the zero and the 5, 10, 15, 20 and 25 ml. graduations, respectively. These corrections are shown graphically in Fig. 74.

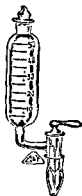


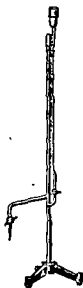
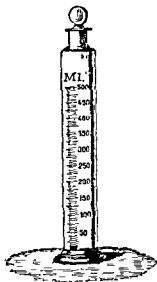
FIG. 75.

In nearly every burette there will be found values for which the graduation is correct. For example, the burette in this special case reads correctly between 0 and 10 ml. In exact work it is advisable to plan the experiment so that the volume of liquid to be taken from the burette is taken from that part of the burette which is correctly graduated.

Weight Burettes should be used for highly accurate work; a

the standard solution used, and in this way drainage and meniscus errors are avoided. Means are provided for completely closing the burette during weighing, so as to prevent evaporation.

**Micro-Burettes.** A convenient and simple type is shown in Fig. 76; it has a total volume of 5 ml. and is graduated in 0.02 ml. The filling-funnel enables the burette tube to be cleaned with a fine brush, but it will usually be found preferable, especially from the point of view of eliminating air-bubbles, to fill the burette by immersing the tip in the solution and

FIG. 76.  
MICRO-  
BURETTEFIG. 77. MEASURING-  
CYLINDER.

applying suction at the wide top end. It is important to note that the glass used for this apparatus should not contain soluble alkali, as this may affect acidimetric determinations. Some micro-burettes have a glass bead inside the rubber tube connecting the jet to the stem, instead of a tap; this enables better control over the size of small drops to be obtained.

### The Measuring-Cylinder

Measuring cylinders of thick glass can often usefully supplement, or replace, measuring flasks, but, since the area of the upper surface of the

liquid in the cylinder is greater than that in the flask, there is a loss of accuracy.

The cylinder is usually graduated throughout the greater part of its length in steps of from 1 to 10 ml., according to its diameter. It may be graduated either for measuring or for delivering a liquid.

Measuring-cylinders are of two kinds. One is narrow at the top, and can be closed by an accurately-ground stopper (Fig. 77). This form is convenient for mixing the liquid contents by shaking, without risk of loss. The other kind of cylinder is wide and open at the top, and is usually provided with a lip.

**Calibration of the Measuring-cylinder.** A cylinder for measuring liquids can be calibrated rapidly by allowing water to flow into it from a previously-calibrated burette. If the graduations are incorrect, it will be necessary to construct a table in which the true value of each graduation is shown, as described above for the burette.

If the cylinder is graduated for "delivering," the interior must be wetted before calibration (see under Measuring-flask, p. 100).

## Solutions

**Standard Solutions.** The solutions of definite concentration which are used in volumetric analysis are termed *Standard Solutions*. A standard solution may be of any known concentration which is suitable for the particular work in hand. A scheme for the correlation of volumetric standard solutions is outlined on p. 100.

**Normal Solutions.** A standard solution is said to be of *Normal* or *Equivalent Strength* when 1 litre of solution contains the equivalent weight in grammes of the active element, acid, alkali, or salt.

By the term "equivalent" is understood the weight in grammes of the substance which is chemically equivalent to 1.008 grm. of hydrogen, to 40.00 grm. of NaOH, to 36.46 grm. of HCl, or to 53.00 grm. of  $\text{Na}_2\text{CO}_3$ , etc.

Thus a normal solution of KOH contains 56.11 grm. of the solid per litre, and a normal solution of  $\text{HNO}_3$  contains 63.02 grm. of the acid in 1 litre of solution. But the normal solution of  $\text{Na}_2\text{CO}_3$  will contain only

$$\frac{106.0}{2} = 53.00 \text{ grm. of the anhydrous salt per litre,}$$

since two molecules of monobasic hydrochloric acid are required to neutralise one molecule of sodium carbonate. Similarly a normal solution of the dibasic sulphuric acid will contain only

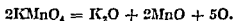
$$\frac{98.08}{2} = 49.04 \text{ grm. per litre.}$$

The capital letter N. is used to denote a normal solution; seminormal, decinormal and centinormal solutions are denoted, respectively, by the symbols 0.5 N., 0.1 N. and 0.01 N. A volume of normal sodium hydroxide solution (or of any base) will exactly neutralise an equal volume of normal sulphuric acid or ten times its own volume of decinormal sulphuric acid (or any other acid).

The principle of equivalence is applied not only to reactions involving



neutralisation, but also to reactions of other types. Thus, when we are considering oxidation, the equivalent weight of a compound is that weight of it which will oxidise 1.008 grm. of hydrogen, or, alternatively, will supply 8.00 grm. of oxygen for oxidation. For example, potassium permanganate in acid solution can supply oxygen according to the following equation :



Thus two molecules of permanganate have five atoms of oxygen available for oxidation. These will be equivalent to ten atoms of hydrogen. Therefore, under the stated conditions, the normal solution of potassium permanganate will contain :

$$\frac{2\text{KMnO}_4}{10} = \frac{316}{10} = 31.6 \text{ grm. per litre.}$$

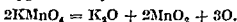
The 0.1 N. solution contains 3.16 grm. per litre.

Similarly, one molecule of potassium dichromate contains three available atoms of oxygen in acid solution, and a normal solution of this salt contains

$$\frac{\text{K}_2\text{Cr}_2\text{O}_7}{6} = \frac{294.2}{6} = 49.03 \text{ grm. per litre.}$$

The 0.1N. solution contains 4.903 grm. per litre.

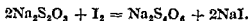
In every case this question of normality must carefully be considered. For example, potassium permanganate in alkaline solution has available only three atoms of oxygen in every two molecules of salt :



Hence the normal solution of permanganate for use in alkaline solution contains

$$\frac{316}{6} = 52.67 \text{ grm.,}$$

not 31.6 grm. of the salt. Similarly sodium thiosulphate reduces iodine as follows :



Hence



so that the normal solution of sodium thiosulphate contains the molecular weight in grammes of the salt, even though it appears at first sight that, because sodium thiosulphate is the salt of a dibasic acid, it should contain only half this quantity.

**Molecular Solution.** A standard solution which contains the molecular weight of the substance in grammes in 1 litre of solution is known as a *Molecular* or *Molar Solution*, and is distinguished by the capital letter M. Solutions of fractional molecular strength are distinguished by the prefixes semi-, deci-, and cent-, and are denoted by 0.5M., 0.1M. and 0.01M., respectively.

### Storage and Preservation of Standard Solutions

Winchester quart bottles are suitable for the storage of standard solutions. The bottle which is to be used should be clean and dry. If

It has been recently washed and is still wet inside, it must be rinsed out with a portion of the standard solution, otherwise the water in the bottle will alter the concentration of the solution. When the solution has been introduced, the bottle should be securely stoppered. It is then immediately labelled with the name of the solution and also its concentration and date of preparation. The label should also be initialled by the person responsible for the contents of the bottle.

Evaporation of water from a standard solution invariably occurs when the bottle is open, and may even take place slowly while the bottle is closed. Some substances in solution also undergo chemical change in course of time. Hence a standard solution usually alters in concentration when it is stored. The amount of this alteration will depend upon the substance dissolved, the age of the solution, and the frequency with which it has been used.

It must further be remembered that, unless the bottle is completely filled, internal evaporation and condensation will cause drops of pure water to form on the upper part of the inside of the bottle. Therefore the bottle must be shaken before removing the stopper.

Loss by evaporation is checked by drawing a tightly-fitting rubber cap or finger-stall over the stopper and neck of the bottle. This not only retains the stopper firmly in its seat, but also forms a covering which keeps the lip of the bottle clean.

Another method of preventing evaporation is to close the bottle with a rubber stopper instead of with an ordinary cork. Or a glass stopper, which is somewhat too small for the neck of the bottle, may be used with a suitable piece of tightly-fitting black rubber tubing drawn over it: the stopper thus acts as a rubber bung. A rubber stopper must always be used for a bottle containing a solution of caustic alkali, because the action of the alkali upon the glass will set a glass stopper fast in its seat. Standard solutions should be kept in a cool place, to minimise evaporation.

Some standard solutions, such as potassium permanganate and silver nitrate, are decomposed by the action of light, and should therefore be kept in the dark. A cool, dark closet or cellar is generally the most suitable place of storage, but if a dark place is not available the bottles may be coated externally with black paint or wrapped with black opaque paper.

Solutions which change rapidly in concentration when exposed to the air, e.g., a solution of sodium hydroxide, are best stored for short periods in the apparatus shown in Fig. 78, p. 135. If sodium hydroxide is being used, the tube at the top of the bottle should be filled with soda-lime, and therefore the alkali will always be out of contact with carbon dioxide while it is standing either in the storage vessel or in the burette.

## SECTION VI

### ALKALIMETRY AND ACIDIMETRY

#### The $P_H$ Notation

A NEUTRAL solution can be defined as a solution in which the concentrations of hydrogen and hydroxyl ions are equal. Thus pure water is neutral and contains approximately  $10^{-7}$  gram. equivalent of both hydron and hydroxyl ion per litre. Their product is  $10^{-14}$  and, according to the Law of Mass Action, whenever water is present the product of the concentrations of the hydron and hydroxyl ions must be  $10^{-14}$ . A solution containing rather more than  $10^{-7}$ , say  $10^{-6}$ , gram. equivalent of hydron will be slightly acid; it will contain  $10^{-8}$  gram. equivalent of hydroxyl ion per litre. Similarly a decinormal solution of hydrochloric acid, assuming complete dissociation, will contain  $10^{-1}$  equivalent of hydron and  $10^{-13}$  of hydroxyl ion; decinormal sodium hydroxide, again assuming complete dissociation, will contain  $10^{-13}$  equivalent of hydron and  $10^{-1}$  of hydroxyl ion.

This method of expressing the concentration of hydrogen ions is a little awkward, and what is known as the " $P_H$  notation" has been introduced to simplify it. According to this notation, a solution containing  $10^{-3}$  gram. equivalents of hydron per litre is said to have a  $P_H$  of 3. The  $P_H$  is thus the common logarithm of the reciprocal of the hydron concentration. In the present example :

$$\log_{10} \frac{1}{10^{-3}} = 3.$$

The  $P_H$  of a decinormal solution of sodium hydroxide will be approximately 13; of pure water, 7; of decinormal hydrochloric acid, 1.

#### Use of Indicators

When an acid is being determined by titration with a standard solution of a base, the object is not to produce a neutral solution, but to add an equivalent quantity of the base to the acid. If the acid and base are both strong, the resulting solution will be neutral; it so happens that in this case the neutral point and the equivalence point are identical. But if we add an equivalent of a strong base, say sodium hydroxide, to a weak acid, say acetic acid, the resulting solution will not be neutral, but alkaline. This can be shown by dissolving sodium acetate in water, when an alkaline solution will be obtained owing to hydrolysis :



The small quantity of acetic acid resulting from the reaction will be almost completely unionised; the sodium hydroxide, on the other hand, will be almost completely ionised, and the solution will contain a small excess of hydroxyl ions. Its  $P_H$  will be greater than 7; it will be alkaline.

Similarly, the salt of a weak base and a strong acid (e.g.,  $\text{CaCl}_2$ ) gives an acidic solution.

Indicators for use in acidimetry are somewhat complex organic compounds which undergo marked colour changes when the  $P_H$  of the solution in which they are present changes. They can therefore be used to measure  $P_H$ , and to show when an equivalent quantity of a base has been added to an acid. Thus, when titrating acetic acid with a solution of sodium hydroxide, the solution will at first be acid, then neutral, and finally, and this before the end-point is reached, alkaline, and an indicator which changes colour at the appropriate alkalinity must be chosen. One which changed colour at  $P_{H7}$ , the neutral point, would be useless in this titration.

A large number of indicators are now available, but, in practice, two only are generally used—methyl orange and phenolphthalein. Methyl orange changes colour in the  $P_H$  range 2.9 to 4.0, i.e., when the solution is still acid. It is therefore useful for the titration of weak bases by strong acids, and, for a reason which will appear later, of strong bases by strong acids. The  $P_H$  range of phenolphthalein is 8.3 to 10.0, and therefore it is suitable for the titration of weak acids by strong bases. As the  $P_H$  of a solution of a weak acid changes only very slowly when a weak base is added, the indicator method is unsuitable for the titration of weak acids by weak bases or *vice versa*.

For the theory of indicators, see *Sutton's Volumetric Analysis* (12th Edition); fluorescent indicators are referred to on p. 253.

Notes on the more important indicators are given below.

**Methyl Orange.** This substance is also known as Helianthin, Tropaeolin D, or Orange III. In acid solution its colour is red; in alkaline, yellow. The  $P_H$  range over which the colour change from red to yellow takes place is 2.9 to 4.0. The indicator is prepared by dissolving 0.05 gm. of the compound in 100 ml. of distilled water. One drop per 100 ml. of solution to be titrated should normally be taken. The colour of methyl orange depends to some extent on its degree of dilution; the more dilute the solution, the more yellow the colour. Therefore it is important that the concentrations of this indicator in the solution under titration and in the solution when the acid or base is being standardised, should be about the same. To obtain the best results with methyl orange, the concentration of acid or base should be comparatively high and the solution should be cold.

The particular virtue of this indicator lies in the fact that it is yellow in all solutions of  $P_H$  greater than 4. Now the  $P_H$  of solutions of weak acids by strong bases is always greater than 4. Therefore, in the titration of weak acids by strong bases, methyl orange behaves exactly as if it were a solution of sodium hydroxide. Moreover, this indicator ignores the accidental introduction of carbon dioxide into standard solutions. Therefore it is used whenever possible in the titration of strong bases by strong acids, of weak bases (e.g., ammonia) by strong acids, and of carbonates by strong acids.

**Phenolphthalein.** The solution of this indicator in neutral alcohol is colourless. When a few drops are added to the solution of an alkali, the liquid assumes an intense red colour; this colour is readily destroyed by the addition of an excess of either mineral or organic acid, and, much less easily, by a large concentration of a strong alkali. A moderate excess of indicator does no harm. Phenolphthalein is suitable for the titration of inorganic and organic acids with strong bases, but it cannot be used in the presence of carbonic acid or of ammonium salts. As it is soluble in alcohol and in alcohol-ether mixtures, it can be used for the determination of organic acids which are insoluble in water.

The presence of free  $\text{CO}_2$  in ordinary distilled water causes a slight error, which should be allowed for, particularly if decinormal acid solution is being used. When a titration is being carried out, the liquids in the titration flask should be mixed by swirling them round. The surface should not be broken, because the absorption of  $\text{CO}_2$  from the air then becomes much more rapid.

of rectified spirit, adding 40 ml. of water and filtering if necessary. The  $\text{P}_H$  range of phenolphthalein is 8.3 to 10.0.

**Litmus.** This is a blue dye-stuff obtainable from lichens, but its principal colouring matter, azolitmin, can now be purchased. An active litmus solution is prepared as follows: Digest the crushed cubes overnight with a 4-fold volume of 85 per cent. alcohol, and pour off and reject the liquid portion. Extract the residue for three successive weeks with 66, 50 and 33 per cent. alcohol, respectively, decanting off the extract at the end of each week. Mix the three extracts, allow them to settle for a further week, and decant off the liquid portion. To 5 ml. of this add 5 ml. of 0.1 N. sulphuric acid, dilute to about 100 ml. and titrate to a purple shade with 0.1 N. alkali. Calculate the amount of nitric acid which must be added to the remainder in order to ensure that in the above titration exactly 5 ml. of 0.1 N. alkali are required. Add this quantity, allow any solid

affected by carbonic acid. The  $\text{P}_H$  of a solution of  $\text{CO}_2$  in water may be taken to be 6. At this value litmus is a purplish colour, neither red nor blue. If, then, a solution of hydrochloric acid contaminated with  $\text{CO}_2$  from the atmosphere is being titrated with pure sodium hydroxide, the hydrochloric acid is first neutralised, but the definite blue, alkaline colour does not appear until the carbonic acid also has been neutralised. The change from red to blue is not sharp, and poor results may be obtained. This difficulty is overcome by boiling the solution to expel the  $\text{CO}_2$ .

An extreme example of the influence of carbonic acid on the colour of litmus is the titration of sodium carbonate with hydrochloric acid. A solution of sodium carbonate has a high  $\text{P}_H$ , and, when litmus is added to it, the solution will be blue. When the hydrochloric acid is run in,  $\text{CO}_2$  will be set free. Much of this  $\text{CO}_2$  will remain in solution, and will act as an acid. The litmus will therefore assume a

**Litmus-paper.** A moderately concentrated solution of purple, neutral litmus solution is prepared, and strips of sized paper are drawn through it. The strips are hung up to dry in a room free from acid fumes. Ordinary sized paper produces a more sensitive test-paper than does filter-paper.

**Methyl Red.** This indicator is suitable for use in the titration of weak organic bases and ammonia. When added in small quantity to an aqueous solution of weak bases it colours the liquid pale yellow, but the addition of a drop of dilute acid in excess changes the colour of the liquid at once to violet-red, and 1 drop of ammonia is then sufficient to render the solution nearly colourless again. Methyl red is not very sensitive to carbonic acid, but it is more sensitive than methyl orange; it is therefore less suitable for the titration of carbonates, but carbonates can be titrated in its presence provided the solution is boiled after each addition of acid, or if the method of back-titration is used (see under Litmus).

The sharp change in colour of this indicator from pale yellow to violet-red

3 drops are added to each 100 ml. of the liquid to be titrated. The  $p_H$  range of methyl red is 4.2 to 6.3.

of paper is wetted with water and one edge is then dipped into a weakly acid solution, we get in succession the yellow colour due to the acid, a brown band due to the water, and the unchanged yellow of the dry paper. This change is very sensitive. Turmeric behaves like phenolphthalein and is used for the titration of weak acids, such as acetic, oxalic and citric, by a strong base. It can be used with highly-coloured solutions, and is used as a test for boric acid in milk.

**Indicator Bottles.** Solutions of indicators should be kept in small, corked bottles. A small groove should be cut in the cork to allow access of air. This is particularly important in the case of litmus, which deteriorates rapidly when kept in a tightly-stoppered bottle. The cork should also carry a small pipette made by drawing out a glass tube at one end. The end of the pipette should reach down to the bottom of the bottle. When some of the indicator is needed, the bottle is tilted at an angle, the tube is closed with a finger, and the pipette and cork are withdrawn. If the closed tube is held almost horizontally over the vessel containing the liquid to be titrated, single drops of the indicator solution can be coaxed out of the pipette by relaxing the finger pressure and increasing slightly the slope of the tube.

### Preparation of Standard Solutions

Many directions and precautions, which are of general importance in the preparation of standard solutions, are given below, and are not repeated. Directions are given for preparing *normal* solutions, but for many purposes solutions of lower concentration are desirable, and for most purposes other *standard* solutions are perfectly satisfactory.

The fetish of normal solutions has gained a firm grip on chemical laboratories. It is very convenient to work with normal solutions because a certain amount of arithmetic is saved when the calculation is made, as a volume of any one normal solution is equivalent to an equal volume of any other normal solution. On the other hand, it is very much easier to make up a standard solution of *approximately* normal concentration. This can usually be made up in one stage and the small, troublesome adjustments needed to bring it exactly to normal, which frequently introduce errors, can be omitted. The great advantage of working with normal solutions, that the weight of a compound *approximately* equivalent to a given volume of a normal solution can quickly be calculated prior to an experiment, is not lost when the solution is only *approximately* normal.

As a general rule the concentrations of solutions and experimental results should be expressed and worked out in grammes per litre and not in terms of normality. The latter system is responsible for many arithmetical errors.

### Normal Sodium Carbonate

This is a semimolecular solution, and contains 53.00 grm. of  $\text{Na}_2\text{CO}_3$  per litre. Pure  $\text{Na}_2\text{CO}_3$  is best obtained by igniting pure sodium bicarbonate.

The bicarbonate should first be tested for traces of chloride and sulphate. The salt is shaken with a small quantity of distilled water in a stoppered bottle. The liquid is filtered, acidified with nitric acid, and the filtrate is tested for foreign radicals. If chloride or sulphate is present, about 100 grm. of the bicarbonate are shaken with a small quantity of distilled water, the salt is allowed to settle, and the liquid is decanted. The washing is repeated with fresh portions of distilled water, until the last washing water gives no reaction for sulphate or chloride; the bicarbonate is then drained on a porous tile and is dried by passing it between dry sheets of filter-paper.

About 9 grm. of the pure bicarbonate, enough to make 100 ml. of the normal solution, are spread in a thin layer inside a platinum or porcelain dish, which is heated over a Bunsen flame to full redness for some ten minutes. If the temperature is allowed to rise too high and a porcelain vessel is being used the carbonate may react with the porcelain, with loss of carbon dioxide. The carbonate will probably sinter, and will then dissolve only slowly in cold water and must be dissolved in hot water in a beaker, as volumetric flasks must not be heated. The solution must then be cooled and transferred to the flask, the beaker being washed out three or four times with cold water.

Alternatively the dish containing the bicarbonate is placed in an air-oven at about  $100^\circ\text{C}$ . The temperature is raised to  $280^\circ$  to  $300^\circ\text{C}$ ., but not higher, for half an hour, and carbonate readily soluble in cold water is thus obtained.

In either case, the heated salt is allowed to cool in a desiccator and is transferred to a dry, stoppered weighing-bottle or tube. The tube and salt are weighed together. Some 5.3 to 5.4 grm. of the salt are needed, and therefore the counterpoising weights are reduced by 5.3 grm. Some of the carbonate is transferred to the beaker or to the measuring-flask, in the latter case through a dry filter-funnel. In either case the vessel should have been brought into the balance-room. The tube is then re-stoppered and its weight quickly estimated. It ought still to be too heavy for the reduced counterpoise. Some more salt is transferred, and so on until the tube is just too light for the counterpoise. The tube is then accurately weighed. After a little practice in this method, it will be found that "weighing out" becomes fast and efficient; one soon learns to guess quantities correctly and to judge reasonably well from the swing of the pointer how far a balance is out of equilibrium.

If a beaker has been used, the carbonate is dissolved in a little hot water and the solution is cooled. This solution, or, in the other case, distilled water, has to be transferred to the 100-ml. flask. This is best done through a funnel which must not fit so well into the neck of the flask that an air-lock is formed. This is ensured by pushing in a small

hook of glass or a bent match-stick between the funnel and the neck. When the flask has been nearly filled, the funnel is washed and withdrawn and the flask is stoppered. Its contents are now mixed by thorough shaking and the solution is made up exactly to 100 ml. by adding water slowly from a wash-bottle with a fine jet, or from a pipette. The bottom of the meniscus must be in line with the graduation mark at the appropriate temperature. The flask is again stoppered and shaken.

As the weight of carbonate used is known, a standard solution has now been prepared. If a normal solution is required, the procedure is as follows: Let the weight of carbonate taken be 5.45 gm. This will make

$$\frac{5.45 \times 1000}{55.00} = 102.8 \text{ ml.}$$

of normal solution. Therefore make up the solution to the 100-ml. graduation mark, add 2.8 ml. of distilled water from a burette, and again mix the contents of the flask by shaking.

flask, and the watch-glass is carefully washed with a jet of water, all washings containing carbonate being added to the contents of the flask.

It will be seen that if one is content with a solution of *approximately* normal concentration, the adjustments with a burette or with a spatula, which may introduce errors and which, at best, are undesirable, are unnecessary.

### Normal Sulphuric Acid

This solution is semimolecular, and should therefore contain 49.04 gm. of  $\text{H}_2\text{SO}_4$  per litre.

The outline of the preparation of the solution is as follows: An appropriate quantity of pure sulphuric acid is diluted with water, by adding the acid to the water. The hot mixture is cooled, and its concentration found by titrating a portion of it with the standard sodium carbonate solution. The amount of water to be added to reduce it to normal concentration may then be calculated.

**Preparation of the Solution.** The sulphuric acid is poured into a measuring-cylinder or into some other vessel of suitable shape. Its specific gravity is then found by a hydrometer (p. 18). Suppose the specific gravity to be 1.69. A reference to the Table on p. 502 will show that sulphuric acid of this specific gravity contains 76.30 per cent. by weight of the pure acid. Hence 1 ml. of the solution weighs 1.69 gm. and contains

$$\frac{1.69 \times 76.30}{100} = 1.29 \text{ gm. of } \text{H}_2\text{SO}_4.$$

For a litre of normal solution 49.04 gm. of  $\text{H}_2\text{SO}_4$  are required. A volume of the solution slightly *larger* than that required is measured out into a cylinder. In this case 35 ml. are required, so take 40 ml. Some 500 ml. of distilled water are then placed in an ungraduated flask



and the sulphuric acid is cautiously added to it. The solution is then cooled and, at the same time, mixed by shaking the flask, while a stream of tap water flows round it. The cooling process can be completed by covering the mouth of the flask with a good-sized inverted beaker, and playing water from the tap on to the bottom of the beaker. If this is done, care must be taken to see that the beaker rests on the top of the neck of the flask, not on the rounded portion. In the latter case the inverted beaker may fill with water and the solution be spoilt.

The cold liquid is transferred to a litre flask, and diluted to 1 litre. After mixing the solution again a portion is titrated with the standard sodium carbonate solution as described below.

**Preliminary Titration of the Acid Solution.** A clean and well-drained 20-ml. pipette is rinsed out, by partly filling it with the normal sodium carbonate solution, shaking the liquid round in the pipette, and allowing it to flow away into the sink. This operation is repeated. The pipette is now once more charged to above the 20-ml. mark with the normal solution and, by carefully relaxing the finger pressure and twisting the barrel, the liquid is allowed to fall to the mark; it is then allowed to flow into a 250-ml. flask or beaker, and it is somewhat diluted with water.

A burette has now to be charged with the diluted acid. If the interior of the burette and the jet are not perfectly dry, they must be rinsed out with a small quantity of the acid, which is rejected. The burette is then filled with the acid, and air bubbles are carefully removed from the tap and jet, by allowing some of the liquid to flow rapidly through to waste.

Sufficient methyl orange solution (1 or 2 drops) is now added to the sodium carbonate solution in the flask to give a pale yellow colour to the liquid. This yellow colour changes to red when the sodium carbonate has been exactly neutralised by the dilute acid from the burette. The flask is placed upon a white plate or tile, and the acid from the burette is dropped gradually into the sodium carbonate solution and is constantly mixed with the solution by shaking it. The addition of acid is continued until the yellow colour of the whole liquid just begins to change to red. It is important that the acid should be added in the slightest possible excess and that the change to permanent red should be produced only on the addition of the last drop of acid. Methyl orange begins to change colour at  $P_H$  4; thus, when an alkali is being titrated with an acid, the end-point comes slightly too late. The first suggestion of a change from yellow to red therefore, should be taken as the end-point. This change is made much more noticeable if in a flask beside the titration flask there is a solution of methyl orange similar in concentration and volume. If the  $P_H$  of this solution is greater than 4, the full yellow colour of the indicator will be developed and the solution will act as a standard of reference. Tap water in volume equal to that of the solution to be titrated frequently serves.

The volume of the dilute acid solution, which has been required for the neutralisation of the sodium carbonate in the flask, is read on the burette, and the result is confirmed by repeating the titration in a precisely similar manner, with a fresh quantity of the sodium carbonate solution. The two titrations should not differ by more than 0.1 ml. To avoid waste of time, it is perhaps better to carry out the first titration rapidly.

This will give him an approximate idea of the end-point. The potassium point is then determined and checked. Three titrations are thus necessary, but each one of these can be carried out rapidly.

**Errors in Analysis.** If a chemical analysis, gravimetric or volumetric, is subject to errors which occur in a haphazard way, the mean of a large number of determinations will probably give a more accurate result than one alone. It would seem, for example, that a much more accurate result is obtained by taking the mean of twenty titrations than from one only. However, it can be shown that if one determination is subject to a certain error, the mean of three will be subject to half that error, of nine to a quarter, and so on. In fact, a point is soon reached when the labour expended in repetition is not worth the extra accuracy achieved. Common sense must be used.

A result based on one solitary titration is worth very little. If it is based on three which do not differ very much among themselves, it is worth a great deal. On the other hand, if the results of the first two titrations are identical, it is often not worth while doing a third, because, even if the third result diverges, the arithmetic mean will not be much altered. These points are discussed further on p. 485. The haphazard errors of a capable chemist are small. On the other hand, if the method and not the worker is at fault, a different method must be sought. Some of the errors inherent in volumetric work may be eliminated by the use of a weight burette (p. 114).

**Process of Dilution to Normal Concentration.** These titrations should have proved that the acid solution is somewhat concentrated. It may be made normal in the manner illustrated by the following example :

In a special case, the 20 ml. of the normal alkaline solution were exactly neutralised by 18.4 ml. of the acid solution. It follows that 18.4 ml. of the acid must be diluted to 20 ml. to provide a normal solution of the acid. A litre of normal acid is therefore made by measuring  $18.4 \times 50 = 920$  ml. of the acid into a litre flask and by diluting this to 1 litre with distilled water. This diluted acid is now thoroughly mixed, and is once more titrated with the alkaline solution, to ensure that no mistakes have been made.

*Note.* If Methyl Red or Litmus is used as the indicator in this titration a somewhat more accurate result will be obtained, but the difference between those

**Titration after Storage.** The acid solution usually alters in concentration after it has been stored for some time. Its concentration must therefore be determined occasionally by titrating it with a freshly-prepared solution of sodium carbonate.

**Other Standard Basic Substances.** The sulphuric acid can be standardised against any other basic substance which can be obtained in a pure state. One such substance is  $\text{KHCO}_3$ ; the requisite quantity of the compound is weighed out directly; it is not converted to the normal carbonate, which is deliquescent.

A second substance is metallic sodium, which can now be obtained in a very pure state. A lump of the metal is quickly cut up into pieces weighing about 0.5 gm. A sodium knife should be used and the metal should never be handled directly with the fingers. It can be lifted

and the  
cooling-

which also serve to absorb any adherent oil. When they are transferred to a clean, dry, stoppered weighing-bottle, they are exposed to the air they will become oxidized. This oxide film will appear to be quite thick, but when the metal is handled at a reasonably fast rate, its oxidation is not serious. It must be remembered that approximately three-fourths of the metal is sodium, and reacts as such.

The sodium and the sodium are weighed, and one lump of the metal is placed in a conical flask, the mouth of which is partially closed with a glass funnel (Fig. 29, p. 32). The tube is reweighed. A small quantity of ethyl alcohol is poured into the flask, where it will react fairly quietly with the sodium to give sodium ethoxide. The alcohol used must not contain much water. When the sodium has dissolved, water is added. This reacts with the sodium ethoxide to produce sodium hydroxide, and, as the weight of this latter compound can be calculated, the sulphuric acid can be standardised. This is a convenient method for obtaining a standard solution of sodium hydroxide free from carbonates.

Guanidine carbonate,  $[\text{NH} : \text{C} : (\text{NH}_2)_2]_2 \cdot \text{H}_2\text{CO}_3$ , is also recommended for standardising sulphuric acid. The molecular weight of this compound is 180.17, and therefore 90.08 gm. of it are equivalent to 1 litre of normal sulphuric acid.

### Normal Sodium Hydroxide

This solution contains 40.00 gm. per litre; it is prepared by dissolving about 44 gm. of sodium hydroxide, "stick soda," in water. The clear solution, after cooling, is transferred to a litre flask and diluted to 1 litre. Twenty millilitres of it are titrated with standard sulphuric acid, with methyl orange as indicator. The standard sodium hydroxide solution is then diluted with water until it is exactly normal, the final solution being checked by another titration.

If the solution must be free from sodium carbonate and from other sodium compounds, a first solution must be made of not less than 10N. concentration; the carbonate will remain undissolved, and is removed by decantation.

If the method of dissolving sodium in alcohol is used, take about 24 gm. of metallic sodium per litre. If the presence of alcohol is undesirable, the sodium is dissolved in a desiccator, from which the stop-cock of which is placed under the sodium, when it is removed and drops into the beaker.

Water, free from carbon dioxide, must be used to dilute the solution of sodium hydroxide. This is best prepared in small quantities by boiling distilled water under reduced pressure (p. 108). If large quantities are required, air freed from  $\text{CO}_2$  by bubbling it through a long column of a dilute solution of sodium hydroxide in a glass cylinder, should be passed through the water. Before entering the water to be purified it should pass through a vertical glass tube about 1 foot long and stuffed with glass wool. This will trap any of the sodium hydroxide solution which has been blown over by the air.

The standard sodium hydroxide solution should never be exposed to the air and should be stored in the apparatus shown in Fig. 78, p. 125, where it is

**Other Standard Acidic Substances.** Certain acidic compounds, which can be prepared in a state of great purity, are available for the standardisation

tion of sodium hydroxide and other alkaline solutions. Of these, potassium bisulphate,  $\text{KHSO}_4$ , which should be used only if it is of analytical grade (p. 520), is probably the most convenient. The molecular weight of this compound is 136.2, and therefore 136.2 gram. of it will exactly neutralise 1 litre of normal sodium hydroxide. Any of the usual indicators can be employed in the titration.

Potassium hydrogen phthalate ( $\text{C}_8\text{H}_5\text{K} \begin{smallmatrix} \text{COOK} \\ \text{COOH} \end{smallmatrix}$ ; 204.2), potassium hydrogen tartrate ( $\text{C}_4\text{H}_4\text{O}_6 \begin{smallmatrix} \text{COOK} \\ \text{COOH} \end{smallmatrix}$ ; 188.2), potassium tetroxalate ( $\text{KH}_2\text{C}_4\text{O}_6 \cdot \text{H}_2\text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ; 254.2), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; 126.1), and benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ; 122.1) are also available. These are all weak acids and, therefore, phenolphthalein must be used as indicator. It must be remembered that phenolphthalein is sensitive to carbon dioxide.

### Normal Hydrochloric Acid

This solution contains 36.46 gram. of  $\text{HCl}$  per litre. A normal solution is best made by measuring the specific gravity of the concentrated acid, referring to the Table (p. 504), and proceeding exactly as is described under the preparation of normal sulphuric acid (p. 123).

**Standardisation of Hydrochloric Acid.** The solution can be standardised against sodium carbonate, or metallic sodium, just as with sulphuric acid; or against a standard solution of sulphuric acid, using an arbitrary solution of a strong alkali of approximately normal concentration as a link. If the alkali is placed in the burette in both cases the burette errors for the two acids will cancel out, and a very exact result will be obtained.

Hydrochloric acid can also be standardised by precipitating the chlorine as silver chloride (p. 74), and weighing the chloride. This method is very exact and links together the two branches of gravimetric and volumetric analysis. Ten millilitres of normal hydrochloric acid should give 1.433 gram. of  $\text{AgCl}$ . As it is inaccurate to take less than 10 ml. of the acid, and as 1.4 gram. of  $\text{AgCl}$  is rather a large quantity of precipitate to handle, the acid should be diluted to 0.1N., when 50 ml. of the solution will yield 0.7167 gram. of silver chloride.

**Standardisation of Hydrochloric Acid with Iceland Spar.** Another excellent method for standardising hydrochloric acid is with Iceland spar, an almost pure, natural calcium carbonate; 50.04 gram. are equivalent to 36.46 gram. of  $\text{HCl}$ , or to 1 litre of the normal acid. Sulphuric acid cannot be standardised by this method, because the  $\text{CaSO}_4$  formed is comparatively insoluble in water.

About 1 gram. of the crushed spar is accurately weighed into a conical flask. A known volume, say 25 ml., of the acid is added, after dilution if necessary. The acid must be in excess. The flask may be warmed to hasten the solution of the carbonate. When all the spar has dissolved, the solution is cooled, and the excess of acid is titrated with any solution of sodium hydroxide of suitable concentration, with methyl orange as indicator. The calcium causes this indicator to fade, and a drop or two

of fresh indicator may be required near the end-point. Finally the same sodium hydroxide solution is titrated against 25 ml. of the acid to be standardised.

In a titration of this type where a considerable amount of preliminary work precedes the actual titration, it is sometimes advisable to transfer a small quantity of the solution which is being titrated to a clean test-tube. This can be done either at the start, or when the behaviour of the indicator shows that the end-point is approaching. The main bulk of the solution is titrated with boldness, and it matters little if the end-point is slightly overshot. The reserve in the test-tube is then added, the liquid from the burette is run in with greater care, and a nearer approximation made to the end-point. Finally the test-tube is washed, the washings being added to the main solution, the flask containing the solution is washed down, and the end-point is accurately determined.

An example to illustrate the method of calculation is given below. The use of the tabular form and of equations in even the simplest exercises in analysis is strongly recommended.

Weight of spar and weighing-bottle = 8.372 grm.

Weight of weighing-bottle = 7.247 "

Weight of spar taken = 1.125 "

Volume of HCl to dissolve spar = 25.00 ml.

Volume of NaOH to neutralise excess of HCl = 4.75 "

Volume of NaOH to neutralise 25 ml. of HCl = 24.15 "

*Acids*

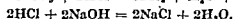
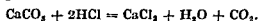
*Bases*

25 ml. HCl 4.75 ml. NaOH + 1.125 grm. CaCO<sub>3</sub>

25 ml. HCl 24.15 ml. NaOH.

Whence (24.15 - 4.75) = 19.40 ml. NaOH  $\equiv$  1.125 grm. CaCO<sub>3</sub>.

and  $\frac{25.00 \times 19.40}{24.15}$  ml. HCl  $\equiv$  1.125 grm. CaCO<sub>3</sub>.



Whence 100.09 grm. CaCO<sub>3</sub>  $\equiv$  36.46  $\times$  2 grm. HCl  $\equiv$  40.00  $\times$  2 grm. NaOH.

Therefore 1.125 grm. CaCO<sub>3</sub>  $\equiv \frac{36.46 \times 2 \times 1.125}{100.09} = 0.8195$  grm. HCl.

Hence weight of HCl per litre =  $\frac{0.8195 \times 24.15 \times 1000}{25 \times 19.40} = 40.81$  grm.

Similarly 1.125 grm. CaCO<sub>3</sub>  $\equiv \frac{40.00 \times 2 \times 1.125}{100.09} = 0.9991$  grm. NaOH,

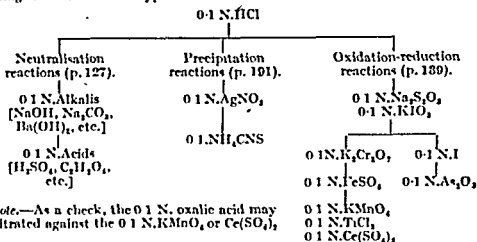
and weight of NaOH per litre =  $\frac{0.9991 \times 1000}{19.40} = 51.50$  grm.

It will be noticed that, incidentally, the sodium hydroxide has also been standardised.

*Note.* The iodate method of standardising acids (p. 180) is both accurate and particularly convenient as a means of linking up neutralisation and oxidation-reduction standardisation methods (see below).

*Correlation of Volumetric Standards.* The following scheme shows how a solution of hydrochloric acid which has been accurately standardised (e.g., by

the gravimetric method, p. 74), may be used as a fundamental standard for all the standard solutions used in the three branches of volumetric analysis. A 0.5 N.HCl solution is stable for long periods and therefore, may be kept for checking purposes only. It is used to prepare a 0.1 N.HCl solution by dilution, and this, the primary working standard, is used as follows to prepare the secondary working standards of each type :—

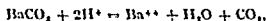


### Determination of a Mixture of Sodium Carbonate and Sodium Hydroxide

A portion of the solution is titrated with standard hydrochloric acid of suitable concentration, using methyl orange as indicator. This gives the total of carbonate and hydroxide. The carbonate in another portion of the solution is precipitated by adding a solution of barium chloride in very slight excess :



The solution is then titrated with the acid, using phenolphthalein as indicator, and the volume of acid used is a measure of the hydroxide present. Phenolphthalein loses its colour when the hydron concentration is lower than that required to attack the precipitate of barium carbonate according to the reaction



and thus it is possible to neutralise the hydroxide with acid without decomposing the carbonate.

Suppose that you are asked to determine the weights of sodium carbonate and sodium hydroxide in a solution, and are told that both compounds are present in approximately seminormal concentration. You are supplied with normal hydrochloric acid.

Pipette 50 ml. of the solution to be analysed into a conical flask, dilute to about 100 ml. and add 1 drop of methyl orange indicator. Titrate with the normal acid until the colour of the solution is no longer a clear yellow, using an alkaline solution of methyl orange as a standard (p. 119). Pipette another 50 ml. of the solution into the conical flask and add about 100 ml. of hot water. Run in a slight excess of barium chloride bench reagent (p. 517) from a burette in volumes of 5 ml. at a time, allowing the precipitate to settle, and noting whether a further quantity of barium chloride causes more precipitate to form. Let the volume used in a special

of fresh indicator may be required near the end-point. Finally the same sodium hydroxide solution is titrated against 25 ml. of the acid to be standardised.

In a titration of this type where a considerable amount of preliminary work precedes the actual titration, it is sometimes advisable to transfer a small quantity of the solution which is being titrated to a clean test-tube. This can be done either at the start, or when the behaviour of the indicator shows that the end-point is approaching. The main bulk of the solution is titrated with boldness, and it matters little if the end-point is slightly overshot. The reserve in the test-tube is then added, the liquid from the burette is run in with greater care, and a nearer approximation made to the end-point. Finally the test-tube is washed, the washings being added to the main solution, the flask containing the solution is washed down, and the end-point is accurately determined.

An example to illustrate the method of calculation is given below. The use of the tabular form and of equations in even the simplest exercises in analysis is strongly recommended.

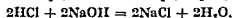
$$\begin{array}{rcl} \text{Weight of spar and weighing-bottle} & = & 8.372 \text{ grm.} \\ \text{Weight of weighing-bottle} & = & 7.247 \text{ ,,} \\ \hline \text{Weight of spar taken} & = & 1.125 \text{ ,,} \end{array}$$

$$\begin{array}{rcl} \text{Volume of HCl to dissolve spar} & = & 25.00 \text{ ml.} \\ \text{Volume of NaOH to neutralise excess of HCl} & = & 4.75 \text{ ,,} \\ \text{Volume of NaOH to neutralise 25 ml. of HCl} & = & 24.15 \text{ ,,} \end{array}$$

<i>Acids</i>	<i>Bases</i>
25 ml. HCl	4.75 ml. NaOH + 1.125 grm. CaCO <sub>3</sub>
25 ml. HCl	24.15 ml. NaOH.

Whence  $(24.15 - 4.75) = 19.40 \text{ ml. NaOH} \equiv 1.125 \text{ grm. CaCO}_3$  ;

and  $\frac{25.00 \times 19.40}{24.15} \text{ ml. HCl} \equiv 1.125 \text{ grm. CaCO}_3$ .



Whence  $100.00 \text{ grm. CaCO}_3 \equiv 36.46 \times 2 \text{ grm. HCl} \equiv 40.00 \times 2 \text{ grm. NaOH}$ .

Therefore  $1.125 \text{ grm. CaCO}_3 \equiv \frac{36.46 \times 2 \times 1.125}{100.00} = 0.8195 \text{ grm. HCl}$ .

Hence weight of HCl per litre  $= \frac{0.8195 \times 24.15 \times 1000}{25 \times 19.40} = 40.81 \text{ grm.}$

Similarly  $1.125 \text{ grm. CaCO}_3 \equiv \frac{40.00 \times 2 \times 1.125}{100.00} = 0.9991 \text{ grm. NaOH}$ ,

and weight of NaOH per litre  $= \frac{0.9991 \times 1000}{19.40} = 51.50 \text{ grm.}$

It will be noticed that, incidentally, the sodium hydroxide has also been standardised.

*Note.* The iodate method of standardising acids (p. 180) is both accurate and particularly convenient as a means of linking up neutralisation and oxidation-reduction standardisation methods (see below).

**Correlation of Volumetric Standards.** The following scheme shows how a solution of hydrochloric acid which has been accurately standardised (e.g., by

the gravimetric method, p. 74), may be used as a fundamental standard for all the standard solutions used in the three branches of volumetric analysis. A 0.5 N.HCl solution is stable for long periods and therefore, may be kept for checking purposes only. It is used to prepare a 0.1 N.HCl solution by dilution, and this, the primary working standard, is used as follows to prepare the secondary working standards of each type :—

## 0.1 N.HCl

Neutralisation reactions (p. 127).

0.1 N. Alkalis  
[NaOH, Na<sub>2</sub>CO<sub>3</sub>,  
Ba(OH)<sub>2</sub>, etc.]0.1 N. Acids  
[H<sub>2</sub>SO<sub>4</sub>, C<sub>2</sub>H<sub>3</sub>O<sub>4</sub>,  
etc.]

Precipitation reactions (p. 101).

0.1 N. AgNO<sub>3</sub>0.1 N. NH<sub>4</sub>CNS

Oxidation-reduction reactions (p. 139).

0.1 N. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
0.1 N. KIO<sub>3</sub>0.1 N. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>0.1 N. FeSO<sub>4</sub>0.1 N. KMnO<sub>4</sub>0.1 N. TiCl<sub>3</sub>0.1 N. Ce(SO<sub>4</sub>)<sub>2</sub>

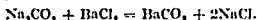
0.1 N. I

0.1 N. As<sub>2</sub>O<sub>3</sub>

Note.—As a check, the 0.1 N. oxalic acid may be titrated against the 0.1 N. KMnO<sub>4</sub> or Ce(SO<sub>4</sub>)<sub>2</sub>.

### Determination of a Mixture of Sodium Carbonate and Sodium Hydroxide

A portion of the solution is titrated with standard hydrochloric acid of suitable concentration, using methyl orange as indicator. This gives the total of carbonate and hydroxide. The carbonate in another portion of the solution is precipitated by adding a solution of barium chloride in very slight excess :



The solution is then titrated with the acid, using phenolphthalein as indicator, and the volume of acid used is a measure of the hydroxide present. Phenolphthalein loses its colour when the hydron concentration is lower than that required to attack the precipitate of barium carbonate according to the reaction



and thus it is possible to neutralise the hydroxide with acid without decomposing the carbonate.

Suppose that you are asked to determine the weights of sodium carbonate and sodium hydroxide in a solution, and are told that both compounds are present in approximately semimolar concentration. You are supplied with normal hydrochloric acid.

Pipette 50 ml. of the solution to be analysed into a conical flask, dilute to about 100 ml. and add 1 drop of methyl orange indicator. Titrate with the normal acid until the colour of the solution is no longer a clear yellow, using an alkaline solution of methyl orange as a standard (p. 110). Pipette another 50 ml. of the solution into the conical flask and add about 100 ml. of hot water. Run in a slight excess of barium chloride reagent (p. 217) from a burette in precipitate to settle, and noting chloride causes more precipitate to



case be more than 15 ml. and less than 20 ml. Now add phenolphthalein and titrate with the acid; assume that 20.5 ml. are required.

If barium chloride is added in considerable excess, it will react with the sodium hydroxide to give barium hydroxide, and poor results will be obtained owing to the rapid absorption of carbon dioxide from the air by this compound. Also, if the precipitation is done in the cold or in the presence of sodium hydroxide, a considerable proportion of basic barium carbonate will be formed. The preliminary result for the sodium hydroxide will be too low for this reason.

Therefore take another 50 ml. of the solution, dilute it to 150 ml. with cold water and run 20.5 ml. of hydrochloric acid slowly into the moving liquid, to avoid any loss of carbon dioxide caused by a high, local concentration of the acid. The solution at this stage should contain all the sodium carbonate, together with a very small quantity of sodium hydroxide. Now heat the solution to about 70° C., run in 20 ml. of the barium chloride solution, add phenolphthalein, and complete the titration. Repeat until concordant results are obtained.

solution is equivalent to 22.4 ml. of N. HCl.

Thus the  $\text{Na}_2\text{CO}_3$  is  $\frac{22.4}{50}$  N.

But N.  $\text{Na}_2\text{CO}_3$  contains 53 grm. of the salt per litre.

Hence  $\frac{22.4}{50}$  N.  $\text{Na}_2\text{CO}_3$  contains  $\frac{22.4 \times 53}{50} = 23.7$  grm.  $\text{Na}_2\text{CO}_3$  per litre.

Similarly the concentration of the sodium hydroxide is

$$\frac{20.8 \times 40.0}{50} = 16.6 \text{ grm. NaOH per litre.}$$

*Note.* The "double indicator" method is sometimes recommended for this determination. The solution is titrated with N. HCl, using phenolphthalein as indicator. This is supposed to lose its colour when all the NaOH has been neutralised and the  $\text{Na}_2\text{CO}_3$  quantitatively converted to  $\text{NaHCO}_3$ . Methyl orange is then added and the titration is completed. This method gives reasonable results provided: (a) The alkaline solution is very dilute and every precaution is taken to prevent premature loss of  $\text{CO}_2$ , for instance by dipping the tip of the burette below the surface of the liquid, and by running the acid slowly into the moving liquid (b) The solution is ice-cold. (c) The solution contains about 20 grm. of NaCl per 100 ml.

It is perhaps better to carry out a titration without precautions other than the prevention of loss of  $\text{CO}_2$ , and then to standardise the acid against a solution containing known concentrations of  $\text{Na}_2\text{CO}_3$  and NaOH, using exactly the same technique as in the determination. The standard solution should be of similar concentration to that of the solution to be analysed.

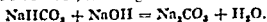
This method, however, is suitable for the determination of small quantities of  $\text{Na}_2\text{CO}_3$  in the presence of much NaOH, since stringent precautions need not then be taken.

### Determination of a Mixture of Sodium Carbonate and Sodium Bicarbonate

For practice, examine commercial sodium sesquicarbonate, which has the approximate formula  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , and use approximately solutions.

Make up a solution of sodium sesquicarbonate containing an accurately weighed quantity of approximately 3.5 gm. of the salt in 500 ml. Titrate 25 ml. of this solution with standard, approximately 0.1 N. HCl, using methyl orange as indicator. The volume of HCl used measures the  $\text{Na}_2\text{CO}_3$  plus the  $\text{NaHCO}_3$ .

To another portion of 25 ml. add, from a burette, 10 ml. of standard approximately 0.1 N. NaOH, to change the bicarbonate into carbonate :



The NaOH must be in slight excess. Dilute to 150 ml., heat to approximately  $70^\circ \text{C}.$ , and from a burette run in bench barium chloride solution diluted ten times. This must be in slight excess (p. 129), or the precipitate will be an indeterminate mixture of barium carbonate and barium bicarbonate and the results will be worthless.

Finally, add phenolphthalein and titrate with the 0.1 N. HCl; 3 or 4 drops of acid should discharge the colour. If more are required too much NaOH has been used, and the precipitate may contain basic barium carbonate. The titrations must then be repeated, using different quantities of sodium hydroxide until the specified conditions are satisfied.

If the solutions of NaOH and HCl are equivalent, the volume of NaOH taken, less the volume of HCl used, is a measure of the  $\text{NaHCO}_3$  present in the salt. The weight of  $\text{Na}_2\text{CO}_3$  is then found by difference.

### Indirect Determination of Barium or Calcium in Solution by Standard Solutions of $\text{Na}_2\text{CO}_3$ and of Acid

The method consists in adding a known volume of decinormal sodium carbonate solution to the neutral solution containing the barium, which is added in quantity more than sufficient to precipitate the whole of the barium as carbonate. To exclude the formation of barium bicarbonate, the solution of the salt should be dilute and at about  $70^\circ \text{C}.$  before the carbonate is added. The excess of sodium carbonate is determined by titration with decinormal acid solution, using phenolphthalein as indicator.

The difference between the original quantity of sodium carbonate taken and the quantity thus found by titration is the weight of  $\text{Na}_2\text{CO}_3$  necessary to precipitate the barium as carbonate; and from this the weight of barium which was originally present in the solution may be calculated as is shown in the following example :

In a special case, the barium was precipitated from solution by adding to it 30.2 ml. of decinormal sodium carbonate. The excess of sodium carbonate required 5.4 ml. of decinormal hydrochloric acid for neutralisation. Now, the phenolphthalein fades when all the sodium carbonate has been converted to bicarbonate.



Thus 5.4 ml. of 0.1 N. HCl are equivalent to 10.8 ml. of 0.1 N.  $\text{Na}_2\text{CO}_3$ . Hence the volume of sodium carbonate solution which was required to precipitate the barium was

$$30.2 - 10.8 = 19.4 \text{ ml.},$$

and each ml. of this solution contains 0.0053 gm. of  $\text{Na}_2\text{CO}_3$ .

Now from the equation,



it will be seen that 157.4 parts by weight of Ba are precipitated by 106.0 parts of  $\text{Na}_2\text{CO}_3$ .

Therefore each ml. of the  $\text{Na}_2\text{CO}_3$  solution corresponds with

$$\frac{137.4 \times 0.0053}{106.0} = 0.00687 \text{ gm. of Ba.}$$

Hence the weight of Ba which was present in the above solution is

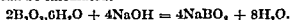
$$19.4 \times 0.00687 = 0.133 \text{ gm.}$$

#### Determination of $\text{B}_2\text{O}_3$ in an Alkali Borate

As free boric acid produces no change in the colour of methyl orange, alkali borates may be titrated with standard acids using this indicator. In other words, solutions of alkali borates react towards the methyl orange as if they are solutions of alkali hydroxides. Since, however, boric acid acts as an acid towards phenolphthalein, the acid may be determined quantitatively by titration

present; this will produce free boric acid corresponding with the borate in the solution.

Now add 50 ml. of glycerol, which must not contain any acidic or alkaline impurity, and titrate the liquid with 0.5 N. NaOH, using phenolphthalein as indicator, until a pink colour appears; then add 10 ml. more glycerol and again add the NaOH until the pink colour reappears. Repeat until the solution remains pink after the addition of more glycerol. From the amount of 0.5 N. NaOH used, the  $\text{B}_2\text{O}_3$  present can be calculated.



*Note 1.* If the borate contains carbonate, neutralise with acid, and boil for a few minutes in a flask fitted with a reflux condenser. The  $\text{CO}_2$  will be driven off, but the slightly volatile boric acid will be condensed and returned. Then rinse the condenser, place the washings in the flask, cool and titrate as before.

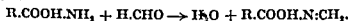
*Note 3.* A better way to bring the solution to the correct  $\text{P}_{\text{H}}$  before titrating the boric acid is to add first a slight excess of dilute HCl, and then an excess of solution containing potassium iodide and potassium iodate in the proportion of 4 parts by weight of the former to 1 part of the latter. This mixture destroys the excess of HCl without reacting with the free boric acid:



The free iodine is destroyed by the careful addition of a very slight excess of sodium thiosulphate solution. After the addition of glycerol the boric acid can be titrated.

#### Determination of Amino Acids

and therefore are normally too weakly acidic to be titrated directly with NaOH, however, an excess of neutralised formalin solution is added, the  $\text{NH}_2$  replaced by the methylene imino group, leaving the  $\text{COOH}$  group available for titration:



The ionisation constant of the compound resulting is about 1,000 times that of the corresponding amino acid, and therefore titration with alkali with phenolphthalein as indicator becomes possible.

**Example.** Prepare a 0.1 N. solution of glycine (monamino acetic acid,  $\text{NH}_2\text{CH}_2\text{COOH}$ ) by dissolving 7.51 gm. in 100 ml. of water. Pipette out 25 ml., add approximately 5 ml. of neutralised formalin, and titrate with 0.1 N. NaOH with phenolphthalein as indicator.

### Direct Determination of Ammonium in its Compounds by Liberating, Absorbing and Titrating the Ammonia

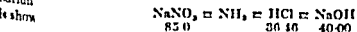
The ammonia, expelled by heating the ammonium compound with a concentrated solution of sodium hydroxide, is absorbed in a known volume of standard acid, and the excess of acid is determined by titration with standard alkali, as has already been described (p. 82); a known volume of standard sulphuric acid is used in the flask (h, Fig. 61, p. 83).

As soon as the evolution and absorption of the ammonia is complete, the absorption apparatus is rinsed out with water, and the acid and washings are made up to a suitable volume. An aliquot portion is titrated with standard sodium hydroxide, using methyl orange as indicator. Two titrations should not differ by more than 0.1 ml. The method is much more rapid than the gravimetric method described on pp. 82—84; it is used in a modified form in the Kjeldahl method for the determination of nitrogen in organic compounds (p. 435).

For practice, determine the percentage of  $\text{NH}_3$  in  $\text{NH}_4\text{Cl}$  by weighing out accurately about 4 gm. of the salt into the distillation-flask. Distil into 100 ml. of approximately normal  $\text{H}_2\text{SO}_4$ . Make up the volume of the distillate to 250 ml. Take an aliquot portion and titrate it with approximately 0.5 N. NaOH.

**Determination of Nitrates by Reduction.** Nitrates can be reduced to ammonia by Devarda's alloy in the presence of a concentrated solution of sodium hydroxide, and the ammonia distilled off and collected in standard acid of suitable concentration (see p. 84). A warning has already been given against distilling over the ammonia too quickly, because then, almost certainly, some of the very concentrated sodium hydroxide will be carried into the standard acid and the titration will be ruined. Example:

**Determination of the Percentage of Sodium Nitrate in Chili Saltpetre**



In a preliminary. The scheme outlined above shows that 85 gm. of  $\text{NaNO}_3$  is equivalent to 30.46 gm. of HCl. As Chili saltpetre generally contains about 50 per cent. of sodium nitrate,  $\frac{85 \times 2}{10} = 17$  gm. of the saltpetre may be equivalent to 1,000 ml. of 0.1 N. HCl.

**Experimental.** About 1 gm. of the saltpetre was weighed out and placed in the reduction flask. It was dissolved in a little water, and about 5 gm. of the finely-crushed Devarda's alloy were added; 100 ml. of 30 per cent. NaOH were slowly added through the funnel. The reaction tended to be violent. After half an hour, half the liquid in the reduction flask was slowly distilled over into 100 ml. of approximately 0.1 N. HCl, tinged with methyl orange. The indicator remained pink.

Then the delivery tubes were washed down with distilled water. The acid was transferred to a measuring flask and made up to 250 ml. Fifty ml. were titrated against approximately 0.05 N. NaOH, using methyl orange.

syphon off the solution into the bottle shown in Fig. 78, and protect it with the soda-lime tube.

Barium hydroxide is best standardised against a standard solution of oxalic acid, using phenolphthalein as indicator.

**Determine the Solubility of Carbon Dioxide in Water.** Put about 150 ml. of distilled water into a clean measuring-cylinder of 500 ml. capacity. Lead a stream of pure carbon dioxide through the water for half an hour. The gas can be generated in a Kipp's apparatus by the action of hydrochloric acid on marble. The gas should be passed in succession through two wash-bottles containing water to remove traces of acid. Stop the stream of gas. Close the cylinder and shake up the liquid with the gaseous  $\text{CO}_2$  which will now have displaced the air in the cylinder. Then pass the gas for five minutes longer, stopper, and shake again. Read the temperature of the solution and the barometric pressure.

Measure out 50 ml. of the approximately 0.1 N.  $\text{Ba}(\text{OH})_2$ , dilute it with 50 ml. of distilled water, and run in 50 ml. of the carbon dioxide solution, which can be taken up in a pipette, provided no great suction is applied. Titrate the excess of  $\text{Ba}(\text{OH})_2$  with standard approximately decinormal oxalic acid, using phenolphthalein as indicator.

Small errors, due to the absorption of  $\text{CO}_2$  from the atmosphere, will have been introduced during this operation. These can be allowed for by taking a second 50 ml. of the  $\text{Ba}(\text{OH})_2$ , diluting with 50 ml. of the same distilled water as was previously used, and titrating with the oxalic acid under exactly the same conditions as before, but without the addition of the solution of carbon dioxide. The difference between the two volumes of acid is a measure of the  $\text{CO}_2$ -content of the water.

Express the results as volumes of  $\text{CO}_2$  corrected at N.T.P., dissolved in unit volume of water. The result can be checked by referring to Tables of Physical Constants containing the solubility of  $\text{CO}_2$  in water under various conditions (see p. 520).

### Determination of Phosphates

The Phosphate is precipitated as Phosphomolybdate; this is dissolved in a measured excess of Sodium Hydroxide, and the excess is titrated with standard Hydrochloric Acid.

The phosphorus is precipitated from a fairly strong solution of nitric acid by a solution of ammonium molybdate in considerable excess. The composition of this precipitate is  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$ .

The procedure for the volumetric method is exactly the same as for the gravimetric determination up to the point at which the phosphorus is completely precipitated (see p. 78). For practice, find the percentage of phosphorus in crystals of potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ .

Weigh out about 1 grm. of the crystals, place them in a measuring-flask of 500 ml. capacity, and make up to the mark with distilled water. Take 50 ml. in a 500-ml. conical flask, and add concentrated  $\text{HNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , and ammonium molybdate as described on p. 79. It is well to precipitate the phosphorus in at least three aliquot portions of the solution, in parallel at the same time.

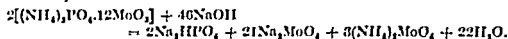
After the precipitates have been allowed to settle in a warm place for one hour, they are filtered through ordinary filter-paper of good quality. They must then be washed free of the nitric acid which is wetting them, but as this cannot be done without removing some of the nitric acid of constitution (see formula) the whole of the nitric acid should, strictly speaking, be removed. The washing liquor is a cold 1 per cent. solution of potassium nitrate in water. Wash each precipitate six times, but make no attempt to transfer the last of the precipitate from the flask to the paper, though, of course, each flask must be rinsed out with this liquor before it is used for washing the paper. Do not try to wash the precipitate until the runnings no longer have an acid reaction. As the phosphomolybdate is slightly soluble in the cold washing-liquor, some of the precipitate is removed by it. On the other hand, traces of acid are left. If the washing is carried out efficiently, to wash six times is a good working compromise.

Then transfer the precipitates with the filter-papers back to their original flasks. To each flask, add 50 ml. of distilled water and 50 ml. of unstandardised sodium hydroxide of about seminormal concentration, so that the sodium hydroxide is in excess. Dissolve the precipitate in the alkali by shaking the flask and breaking up the filter-paper with a glass rod. Make sure that no precipitate, particularly that at the apex of the paper, remains undissolved. Add 10 drops of phenolphthalein, and titrate with standard approximately 0.5 N. HCl.

Find the volume of the HCl equivalent to 25 ml. of the NaOH by titrating that volume of alkali under similar conditions.

The weight of HCl equivalent to the phosphorus can be calculated from the results.

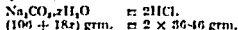
The equation is :



Whence  $2\text{P} = 46\text{NaOH} = 46\text{HCl}$ ; or 30.98 grm. P =  $23 \times 36.43$  grm. HCl.

Other determinations which involve the use of standard acids and alkalis.

(a) Determine the number of Molecules of Water in Washing-Soda ( $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ ). Weigh out successively, portions of about 3 grm. of washing-soda. Dissolve them in water and titrate with HCl of approximately normal concentration, using methyl orange as indicator.



From the results,  $x$  can be calculated.

(b) Determine the percentage of Phosphoric Acid in a mixture of Phosphoric and Sulphuric Acids. Titrate a suitable volume of the mixture with standard

(c) Identify the Potassium Oxalate provided. The salt may be either  $\text{KHC}_2\text{O}_4$ , the binoxalate; or  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , the tetroxalate or quadroxalate. The equivalent weights, respectively, are 125.1 and 84.7.

Make up a standard solution of the salt and titrate it with standard NaOH, using phenolphthalein as indicator.

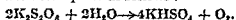
(d) Determine the percentage of Calcium Oxalate in a sample of that Salt.  
orange.

If the sample of oxalate contains carbonate, dissolve a known weight of it in the HCl, boil to expel CO<sub>2</sub>, cool the solution, and titrate the excess of HCl with the NaOH, using litmus as indicator. From the result, the percentage

turns yellow. Litmus must also be used in the second experiment to maintain the similarity of conditions.

(e) Determine the Total Acid in Vinegar. The acid content of most samples of vinegar is approximately 6 per cent., and most of this is acetic acid (eq. wt. 60). Vinegar is therefore an approximately normal acid. In the determination, take 25 ml. of vinegar, add a few drops of phenolphthalein, which must be used because acetic is a weak acid, and titrate with standard NaOH of approximately normal concentration.

(f) Determine the percentage of Potassium Persulphate in a sample of that Salt. If a solution of potassium persulphate is boiled in the presence of a suitable catalyst, the salt decomposes as follows :



Weigh out accurately about 0.4 gm. of the persulphate and dissolve it in about 30 ml. of cold water. Add methyl orange and, if the indicator goes red, bring back the yellow colour with decinormal sodium hydroxide. The volume of this solution used is a measure of the quantity of potassium bisulphate originally present in the potassium persulphate.

Now add 5 drops of decinormal silver nitrate solution, and boil for twenty minutes. Cool, add more methyl orange, and titrate with the standard sodium hydroxide.

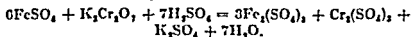
When a solution of ammonium persulphate is boiled, the decomposition is complex, some nitric acid being formed. Ammonium persulphate, therefore, cannot be determined by this method.

## SECTION VII

### PROCESSES OF OXIDATION AND REDUCTION

#### Use of Potassium Dichromate Solution

POTASSIUM dichromate contains oxygen available for the oxidation of various substances, and in the process of oxidation it is itself reduced to a mixture of potassium and chromic salts. Advantage is taken of this reaction to determine ferrous salts and other easily-oxidisable substances. It must be clearly recognised that potassium dichromate loses its available oxygen only in the presence of a substance capable of receiving it, and in the presence of a liberal excess of sulphuric or hydrochloric acid. Thus a ferrous salt in an acidified solution is at once converted into ferric salt by the addition of a solution of potassium dichromate. The reaction is :



From this equation it follows that 294.2 grm. of potassium dichromate can convert  $6 \times 55.84 = 335.0$  grm. of iron from the ferrous to the ferric state, provided that sufficient acid is present.

Because potassium dichromate is reddish-yellow in colour, and is reduced to a green chromium salt, the point at which a slight excess of dichromate has been added to the ferrous salt cannot readily be seen, and an indicator such as potassium ferricyanide solution must be used.

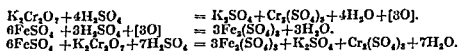
Ferrous salts give, but ferric salts do not give, a blue precipitate with this reagent. The dichromate solution is accordingly added to the acidified iron solution, until a drop of the liquid ceases to give a blue coloration when it is brought into contact with a drop of potassium ferricyanide solution on a glazed white tile.

Crystals of potassium ferricyanide which have been stored in the laboratory are often covered with a layer of potassium ferrocyanide. As this ferrocyanide reacts with ferric iron to give a blue coloration, the indicator will not work sharply unless this salt is completely absent. A good way to prepare the indicator is to crush a large ferricyanide crystal in a mortar. The fragments are transferred to a test-tube, and are shaken repeatedly with successive volumes of distilled water until a piece about the size of a pea is left. This is dissolved in about 10 ml. of water. The solution prepared in this manner must be kept clean and free from reducing agents. It may fail to give distinct colours after it has been kept for about an hour. A fresh solution must then be made. It is important to pay the the greatest attention to the preparation of this indicator.

*Note 1.* The detection of the complete oxidation of a ferrous salt solution is much simpler when standard permanganate solution is used instead of dichromate, since the coloration of the liquid itself becomes the indicator. However, the use of permanganate is inadmissible in the presence of readily oxidisable organic matter, and is possible only under special conditions when hydrochloric acid is present.

*Note 2.* The equation for the oxidation of a ferrous salt by potassium dichromate can be set out in three stages as follows :





From the above, it is seen that the molecule of  $\text{K}_2\text{Cr}_2\text{O}_7$  contains 3 atoms of oxygen available for oxidising purposes, though it will not give up this oxygen unless a substance which can be oxidised is present and the conditions are otherwise suitable. The equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is therefore one-sixth of the molecular weight, and a normal solution will contain

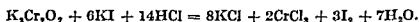
$$\frac{294.2}{6} = 49.03 \text{ grm.}$$

of the salt per litre of solution.

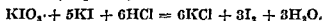
**Preparation of the Dichromate Solution.** It is customary to use standard solutions of approximately decinormal concentration in oxidation and reduction processes. Such a solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  will contain about 4.9 grm. per litre (see *Note 2* above).

As the salt can now be bought under a guarantee of purity, it is sufficient to heat the crystals at  $150^\circ \text{C}$ . until they are perfectly dry. They are then weighed out accurately, dissolved in water, and made up to a known volume. Such a solution need not be further standardised.

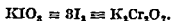
The solution must be re-standardised after it has been kept for some time against a standard solution of ferrous iron, made by dissolving a known weight of ferrous ammonium sulphate in dilute sulphuric acid. Alternatively the ferrous solution may be prepared by dissolving pure iron in dilute sulphuric acid. Another way of standardising the dichromate is to allow it to react with an excess of potassium iodide in the presence of hydrochloric acid.



The iodine is then titrated with an arbitrary solution of sodium thiosulphate (p. 162). Next, a solution containing a known weight of potassium iodate, a salt easily obtained in a state of the highest purity, is also allowed to react with potassium iodide (cf. p. 163).



This iodine is also titrated with the same sodium thiosulphate. From the results, the concentration of the dichromate can be calculated, because :



That is, 214.0 grm. of  $\text{KIO}_3$  can oxidise the same weight of hydriodic acid as can 294.2 grm. of  $\text{K}_2\text{Cr}_2\text{O}_7$ .

**Standardisation of Dichromate Solution by Ferrous Ammonium Sulphate.** The formula of this salt is  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , and its molecular weight is 392.1. Its equivalent weight is the same as its molecular weight, and therefore a decinormal solution will contain 39.21 grm. of the salt per litre. Note that almost exactly one-seventh of the salt is iron. Two methods are described :—

(1) Make up a solution of ferrous ammonium sulphate of approximately decinormal concentration by weighing out accurately about 10 grm. of the salt and transferring to a 250-ml. flask. The salt is somewhat easily hydrolysed by pure water to produce an insoluble basic salt. The hydrolysis is quite easily prevented by the presence of a small quantity

of dilute sulphuric acid, and therefore the crystals should be wetted with a few millilitres of this acid before the water is added. On the other hand, it is most difficult, once the basic salt has been formed, to get the iron to redissolve. As the presence of a considerable quantity of acid will not interfere in the determination, it is therefore good policy to make liberal use of dilute sulphuric acid when handling ferrous ammonium sulphate. In very accurate work, air-free water should be used to make up the volume to 250 ml., but this precaution is not otherwise necessary.

Take 25 ml. of the standard iron solution in a conical flask, add more dilute sulphuric acid if necessary, and dilute with water to about 100 ml. Place 5 separate drops of the ferricyanide indicator on a white tile in an orderly row. Run in 5 ml. of the dichromate from a burette, shake to mix, withdraw a drop on a glass rod and add this drop to one of the drops of ferricyanide on the tile. If a blue colour or precipitate is seen, add an additional 5 ml. of dichromate, test again, and so on, adding the dichromate in volumes of 5 ml. at a time until only a reddish-brown colour is seen on the tile. In this way a large "bracket" can be obtained in a short time. Suppose the "bracket" to be 20 to 25 ml., 20 ml. of the dichromate being too small a volume and 25 ml. too large. Now take a second volume of 25 ml. of the ferrous solution and prepare the solution for titration as before. Run in 21 ml. of the dichromate, test; add an additional 1 ml., test; and so on, until the new "bracket" is made. Let it be 22 to 23 ml. Take a third volume of the iron solution, run in 22 ml., test, and then add the dichromate 2 drops (0.1 ml.) at a time until the disappearance of the blue colour on the tile. Check the last result by a fourth titration. Note that only a small number of drops of ferricyanide indicator should be put out on the tile at one time; the quality of the drops deteriorates rapidly. Note also that the glass rod must be washed in iron-free water every time it is used. In some localities, tap water is suitable; in others distilled water must be used. It is bad practice to dip the rod into a vessel containing distilled water; the traces of iron which soon accumulate in this water interfere with the end-point. Wash either in running tap water or by squirting a jet of distilled water from a wash-bottle along the rod.

It would appear at first sight that much time will be spent in making the "brackets" required by the system of titration described above. This is not so, and in this particular case the method gives a result in much shorter time than would be required to "creep" to the end-point. When using an external indicator, always "bracket." With internal indicators, provided the initial titration is carried out speedily, the system may not save time.

(2) Alternatively, weigh out accurately successive lots of about 1 gram. of the ferrous salt, dissolve these separately in dilute sulphuric acid and titrate as before. As the weight of each portion will be slightly different, it is advisable to arrange them in order of their weights and to titrate the smallest quantity of salt first, adding the dichromate, as previously, in volumes of 5 ml. Suppose the "bracket" is again 20 to 25 ml. Then certainly more than 20 ml. of the solution will be required for the next smallest quantity of salt, and so on. Alternatively, the approximate volume of solution equivalent to a given weight of salt can rapidly be calculated. A slide-rule is useful for such calculations.

When a considerable weight of salt is to be used in each titration, this

method of weighing out successive lots is preferable to weighing out one portion and making it up to a standard volume in a measuring-flask. Weighing may be rapid, as no great accuracy is required; the nearest 5 milligrams suffices. An error of 5 milligrams on 1 gm. is an error of 1:200; this is permissible in most volumetric analyses. This error will be introduced only if one titration is made; a second, check titration will almost certainly reduce it. The advantages of the method are that comparatively small quantities of material have to be handled at any one time, and also that an error in weighing is unlikely to pass undetected, as the weighings are made three or four times.

**Standardisation of the Dichromate Solution by means of Metallic Iron.** A known weight of pure iron is dissolved in dilute sulphuric acid, in the absence of air, in the following way:

*Preparation of the Solution of Iron.* Weigh out accurately about 1.5 gm. of

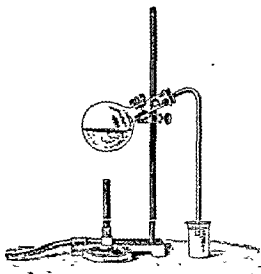


FIG. 79. SOLUTION OF IRON.



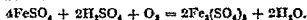
FIG. 80. HUNSEN VALVE.

Armed iron. This should be in the form of small pieces of wire, the wire, before cutting, having been freed from rust by cleaning it with emery-paper.

Fit a 300-ml. round flask with a perforated cork, through which a bent glass delivery-tube passes (Fig. 79). One end of this tube terminates just below the cork, while the other end dips below the surface of a little water contained in a small beaker. Support the flask in an inclined position, as shown.

Now half fill the flask with dilute sulphuric acid, drop in a small piece of pure crystallised sodium carbonate, and replace the cork and tube. The carbonate will dissolve, evolving carbon dioxide, which will replace the air in the flask. When the effervescence has nearly ceased, add the weighed iron. Then fit in the cork and tube, and heat gently by means of a small flame, until the iron is dissolved as ferrous sulphate and no more hydrogen escapes through the water in the beaker.

The exclusion of air during this process is necessary, in order to prevent the formation of ferric salt:



The ease with which a solution of ferrous sulphate is oxidised by the air or even by other oxidising agents, such as dilute nitric acid, has been greatly overestimated in the past. If any chlorine ion is present, however, oxidation may proceed rapidly.

Test these statements by weighing out two more lots of 1.5 gm. of the pure iron and dissolving the first in dilute sulphuric acid as above, but in an open

conical flask, and the second in dilute hydrochloric acid in a similar flask. Titrate both solutions with potassium dichromate of approximately decinormal concentration, as described below.

Another device, which allows the hydrogen gas to escape from the flask and at the same time prevents the entrance of air, is the Bunsen valve. This is shown in Fig. 80. The neck of the flask is stoppered with a cork which carries a short glass tube, as shown. The upper end of this tube is capped by a small piece of rubber tube, the top end of which is closed by a small piece of glass rod. A vertical slit is made in the rubber tube. This slit is easily opened by the pressure of hydrogen gas from within, but pressure from without closes it, and therefore air cannot enter the flask.

While the iron is dissolving, prepare some cold water free from dissolved oxygen (p. 109). As soon as the iron has gone into solution, cool the liquid, transfer it to a 250-ml. flask, and rinse out the round flask several times into the measuring-flask with air-free water. Finally, make up the solution to the mark with the air-free water, mix by shaking, and titrate one-tenth with the solution of potassium dichromate, using potassium ferrieyanide as external indicator.

*Example.*—1.152 gm. of Armco iron were dissolved in acid and the solution was made up to 250 ml.

25 ml. of this solution required 21.1 ml. of the dichromate solution in order to convert the ferrous into ferric salt.

Therefore 211 ml. of the dichromate solution correspond with 1.152 gm. of iron.

And 1000 ml. of dichromate solution will therefore correspond with

$$\frac{1.152 \times 1000}{211} = 5.460 \text{ gm. of iron.}$$

Or, as 55.84  $\times$  6 gm. of iron are equivalent to 291.2 gm. of  $K_2Cr_2O_7$ , the concentration is

$$\frac{291.2 \times 5.46}{55.84 \times 6} = 4.80 \text{ gm. of } K_2Cr_2O_7 \text{, per litre.}$$

### Internal Oxidation-Reduction Indicators

These indicators have been introduced to mark the end-point in titrations with potassium dichromate and similar reagents. Their use results in a certain saving of time, but they are not so reliable as ferrieyanide. An elementary treatment of their mode of action is given below.

It is possible to find a substance, oxalic acid, for example, which is easily oxidised by permanganate, but not by dichromate or ferric chloride, and also one which is oxidised by both permanganate and dichromate, but not by ferric chloride. This is merely a statement of the familiar idea that some oxidising agents are stronger than others. But such a statement is not the whole truth, because the oxidising power of a solution containing an oxidising agent depends not only on the nature of the compound, but also on the *ratio* of the concentrations of the oxidised form and the reduced form of the compound. It is practically independent of the absolute concentration of the oxidised form (see also p. 214). Thus if a solution containing 10 gm. of iron as ferric chloride is added to an excess of a solution of a reducing agent, R, the power of the iron solution to oxidise will decrease as ferrous iron is produced, and it may be that when ten-elevenths of the iron have been reduced, the remaining ferric iron will be unable to oxidise R, because the ferric-ferrous ratio has fallen to 1 : 10; the reaction has become balanced. If 1 gm. only of iron as ferric chloride had been added to the solution of R, oxidation of R would again have taken place until  $Fe^{+++} : Fe^{++} :: 1 : 10$ , when further oxidation would have ceased. If an equivalent quantity of potassium dichromate

had been added to R, more of R would have been oxidised, because dichromate is a stronger oxidising agent than ferric chloride, but again oxidation would have ceased at some  $\text{Cr}^{+++} : \text{Cr}_2\text{O}_7^{--}$  ratio. That this ratio may be very large indeed (i.e., that the dichromate may have been practically quantitatively reduced), does not affect the argument.

If a solution of ferrous chloride is titrated with potassium dichromate, the oxidising power of the solution will increase fairly slowly on the whole, because the ratio of the concentrations of ferric and ferrous ions will be increasing fairly slowly. Near the end-point, however, this ratio will increase rapidly, and consequently the oxidising power also will be increasing rapidly. Directly the dichromate is in slight excess, there will be a further large increase in oxidising power. Now if in this solution there is a compound which is not oxidised until practically the whole of the iron has been converted to the ferric state, and if the oxidation of this compound is accompanied by a marked colour change, then the substance can be used as an internal indicator.

Several such compounds have been found to behave somewhat in the way outlined above. Of these, only two, barium diphenylamine sulphonate,  $[(\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{SO}_3)_2\text{Ba}]$ , and tri-ortho-phenanthroline ferrous sulphate, commonly known as ferrous phenanthroline,  $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{SO}_4]$  will be discussed here, but others will be mentioned later (p. 200). The barium diphenylamine sulphonate is pale green in colour in the presence of a reducing agent, but an oxidising agent will transform it to a compound of an intense purple-blue colour. Unfortunately this salt is somewhat easily oxidised. If used to show the end-point when ferrous iron is being oxidised with potassium dichromate, the purple colour will normally appear before all the iron is oxidised. That is to say, a solution containing a ratio of perhaps 10 ferric ions to 1 ferrous ion has a sufficiently strong oxidising power to change the indicator. The indicator would therefore appear to be useless, but it is known that a solution of ferric phosphate in a mineral acid is inappreciably ionised and if, therefore, a considerable quantity of orthophosphoric acid is added to the ferrous solution before titration, a large proportion of the ferric iron will be removed as ferric phosphate and the ratio of ferric to ferrous ions will remain low until the concentration of ferrous ions becomes very small. In other words, the barium diphenylamine sulphonate can be used as an internal indicator in this reaction, provided a considerable quantity of orthophosphoric acid is present.

The ferrous phenanthroline, on the other hand, is somewhat difficult to oxidise. The reduced form of the indicator is a deep brown-red; the oxidised form a moderately intense green. If used in the above reaction, the red colour will not disappear sharply. A considerable time is required for a small excess of dichromate to produce the green form, and, in practice, it is easy to add too much dichromate, and the end-point is unsatisfactory. On the other hand, the oxidised form of this indicator is quite easily reduced by ferrous sulphate, and a good end-point is obtained by running the ferrous solution into the oxidising agent. Thus, in the determination of ferrous iron, accurate results can be obtained rapidly with this indicator by adding an excess of standard potassium dichromate to the solution of ferrous iron to be determined and titrating this excess with a standard solution of ferrous sulphate.

## Notes on Oxidation-Reduction Indicators

**Barium Diphenylamine Sulphonate.** An aqueous solution containing 3-17 gm. of the salt per litre should be used. The optimum conditions for the titration of ferrous iron by potassium dichromate are: The sulphuric acid concentration of the solution to be titrated should be approximately normal, although satisfactory results can be obtained if the sulphuric acid content varies between 0.25 N. and 3 N. To every 50 ml. of solution in the titration-flask add 10 ml. of a 25 per cent. solution of orthophosphoric acid. Use 5 drops of the indicator for decinormal iron solutions, and 1 drop for more dilute solutions. In the case of decinormal solutions, the indicator correction is negligible; for centinormal solutions it is approximately 0.3 ml., but this may be eliminated by standardising the dichromate against a standard solution of ferrous ammonium sulphate under exactly the same conditions as those under which the determination will be carried out.

The use of hydrochloric acid in concentrations similar to those given above for sulphuric acid, though not altogether advisable, is admissible; since, therefore, tin and mercury do not interfere, the determination of iron by reduction with stannous chloride and re-oxidation by dichromate is possible if this indicator is used. Zinc sulphate does not affect it.

**Ferrous Phenanthroline.** Use 1 drop of an aqueous solution containing 5 gm. of *o*-phenanthroline monohydrate and 7 gm. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per litre. When determining ferrous iron with dichromate, the titration goes most smoothly when 25 ml. of a decinormal solution of potassium dichromate are diluted to 100 to 300 ml., the sulphuric or hydrochloric acid content is raised to 0.5-3 N., and the ferrous sulphate is run into the dichromate. Under these conditions, the presence of orthophosphoric acid is unnecessary. Neither zinc sulphate or chloride, nor stannic chloride or mercuric chloride interferes.

When using this indicator in the determination of ferrous iron with permanganate the concentration of the chloride ions should be as low as possible, the permanganate should be run into the ferrous solution, and the solution to be titrated should contain 10 ml. of 25 per cent. orthophosphoric acid per 50 ml. of solution. A more accurate result will be obtained in this method if a considerable quantity of manganese sulphate is also present (p. 157).

Diphenylamine dissolved in concentrated  $\text{H}_2\text{SO}_4$  is frequently recommended as an oxidation-reduction indicator, especially for iron titrations. The two indicators described above are, however, preferable. It should be noted that the diphenylamine is oxidised to diphenylbenzidine, and that this is the true indicator; it is in fact used directly in zinc ferrocyanide titrations (p. 200).

### Determination of Iron in Ferrous and Ferric Compounds by means of Standard Dichromate

The total amount of iron present in an iron compound may be determined by means of standard potassium dichromate solution.

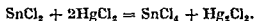
If ferrous compounds only are present, the solution may be titrated at once by the process described on p. 140. If the iron is present in the ferric state only, it is first reduced to the ferrous state, and the ferrous salt is then titrated. If the iron is present both as ferrous and ferric, the amount

of ferrous iron in one portion of the solution is first determined by dichromate; and the whole of the iron in another portion of the solution is then reduced and determined. The difference between the two quantities of iron found will give the weight of iron which was originally present as ferric iron.

**Determination of Iron in Ferric Compounds.** Methods are described below for the reduction of the iron to the ferrous state. The first of these is generally considered to be the best, but its use is not always permissible (see p. 150).

For practice, dissolve 10 gramm. of iron alum,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , in water containing about 30 ml. of dilute  $\text{H}_2\text{SO}_4$ , and dilute to 250 ml. Reduce the ferric salt in the solution to ferrous salt, and titrate the iron with the dichromate solution.

**Reduction by Stannous Chloride Solution.** The iron in the acidified iron solution is reduced to the ferrous state by the addition of stannous chloride solution, which must be added in slight excess (*Note*). The excess of the stannous salt is then converted into stannic salt by adding excess of mercuric chloride solution:



Twenty-five millilitres of the iron solution are placed in a conical flask, 2 ml. of concentrated hydrochloric acid are added, and the liquid is heated to boiling. A clear, freshly-made, dilute solution of stannous chloride is run in from a burette. It is often convenient to use an approximately normal solution of stannous chloride made by dissolving 6 gramm. of tin-foil in 50 ml. of concentrated hydrochloric acid, or 10 gramm. of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 25 ml. of concentrated hydrochloric acid and, in either case, diluting the solution to 100 ml. The stannous solution is added drop by drop, until the yellow colour of the iron solution just disappears. The volume of stannous chloride used is noted, because a knowledge of this volume is of value when the reduction of a second and third portion of the ferric solution is being carried out. The solution is then cooled. About 3 ml. of a saturated solution of mercuric chloride are added. This must produce turbidity in the liquid (due to mercurous chloride), indicating that the stannous chloride has been added in excess. The mercuric chloride must also be in excess. The solution is then titrated. If a considerable quantity of mercurous chloride is produced, a smaller quantity of stannous chloride must be taken for the next reduction.

*Note.* If a large excess of  $\text{SnCl}_2$  solution is added, a very large quantity of  $\text{Hg}_2\text{Cl}_2$  solution will be required, and the precipitate of  $\text{Hg}_2\text{Cl}_2$  will interfere with the titration. If the white precipitate of  $\text{Hg}_2\text{Cl}_2$  turns grey, it is a sign that too much stannous chloride has been used, or that the solution was too hot when the mercuric salt was added. The grey colour is due to the presence of finely-divided mercury. This will probably cause erroneous results. This method of reduction is fast and accurate if carefully-carried out, but it is not suitable for iron solutions which are coloured brown with organic matter.

**Reduction with Sulphurous Acid.** Put 25 ml. of the ferric solution into a conical flask and add ammonium hydroxide gradually until a slight, permanent precipitate is produced. Add 25 ml. of water saturated with sulphur dioxide, and 50 ml. of distilled water. Introduce some

pieces of porous pot into the flask to reduce bumping, and boil to complete the reduction and to expel excess of  $\text{SO}_2$ . The solution should be quite free from any tinge of yellow and should give no reaction with KCNS. The reduction will not take place at all readily if the concentration of mineral acid, particularly of hydrochloric acid, is high. Neither will the reduction take place in alkaline solutions. When all the  $\text{SO}_2$  has been expelled, add 10 ml. of dilute sulphuric acid before titrating.

The quantitative removal of the  $\text{SO}_2$  takes a long time, even if the liquid is boiling briskly. About one-third of the liquid in the flask must normally be evaporated before the  $\text{SO}_2$  is expelled, but the process is speeded up if a current of  $\text{CO}_2$  is passed through the boiling liquid. Probably the best way to test for traces of  $\text{SO}_2$  in the escaping gases is to fit the flask with a cork and delivery tube, and to pass the gases through a very dilute solution of potassium permanganate, which they decolorise. The cork should be in place only when the test is being carried out.

**Reduction by Zinc.** Three methods of reduction which involve the use of zinc are practised. The first is with zinc and sulphuric acid, the second with a solution of zinc in mercury (zinc amalgam), the third with amalgamated zinc in the Jones reductor. Zinc should not be used as the reducing agent when potassium ferricyanide indicator is to be used later, because of the formation of insoluble, bluish zinc ferricyanide.

**Use of Granulated Zinc.** The metal should be free from iron and carbon. Zinc is sometimes so pure that it will dissolve in acids only with difficulty. In this event, it should be melted with 1 per cent. of its weight of aluminium and re-granulated.

Place 25 ml. of the iron solution in a conical flask and add a considerable excess of granulated zinc. This excess is necessary because the reduction appears to take place only on the surface of the metal, and, if only a small area is available, reduction will be slow. Add about 40 ml. of 25 per cent. sulphuric acid. Warm gently and allow to stand. The zinc will dissolve in the acid with evolution of hydrogen, and a portion of this hydrogen will react with the ferric salt, and reduce it. As the escaping bubbles of hydrogen tend to carry away iron, loss must be prevented by partially closing the mouth of the flask with a small funnel (Fig. 29, p. 32). After a time, the colour of the solution will change from yellow to pale green. If the evolution of hydrogen is very slow, the reduction may be hastened by the addition of 3 drops of a concentrated solution of copper sulphate.

Before determining the iron, make sure that it is present entirely in the ferrous state by taking out a drop of the solution with a clean glass rod and bringing it into contact with a drop of potassium thiocyanate solution on a white tile or dish. No red colour should appear, or at most only a faint pink tint. If a distinct red colour is produced, the reduction must be continued, more zinc or acid being added if necessary. The solution is again tested with the thiocyanate, and these operations must be repeated until no ferric salt can be detected.

When the whole of the iron is reduced, the liquid is cooled quickly, and the zinc is removed by placing a small plug of glass wool in the stem of a filter-funnel, and filtering the cold liquid rapidly through the wool into a second conical flask. The funnel and the reduction vessel are then rinsed several times with water.



**Use of Zinc Amalgam.** Reduction with zinc amalgam is much faster than reduction with zinc and sulphuric acid, and, as no hydrogen is evolved, there is no waste of metal. The amalgam can therefore be used repeatedly.

The amalgam is prepared by heating together 4 grm. of granulated zinc, 100 grm. of mercury and 20 ml. of dilute sulphuric acid for one hour in a conical flask on a water-bath. It is then washed with water and filtered through glass wool into a bottle with a well-fitting glass stopper. The capacity of the bottle should be 150 to 200 ml.

Place 25 ml. of the ferric solution in the amalgam-bottle with 25 ml. of 20 per cent. sulphuric acid. Stopper, and shake vigorously for one minute. Pour off the solution into a flask, taking care to keep back all the amalgam. Add a further 25 ml. of the acid to the amalgam, wash down the stopper and neck of the bottle, stopper, and shake. Add this washing liquid to the reduced iron solution. Repeat the washing.

If water is used for removing the last-traces of iron from the bottle, basic salts, which are slightly oxidised by potassium permanganate and which therefore lead to slightly high values, are formed.

**Use of the Jones Reductor.** This apparatus is shown in Fig. 81. It consists of a glass tube about 40 cm. in length and 2 cm. in diameter, and to one end of it is sealed a narrow glass tube carrying a stop-cock. For convenience in filling, the top end of the main tube is blown out into a cup of about 50 ml. capacity. At A there is a perforated porcelain disc which is covered either with a thin layer of ignited asbestos or a thicker layer of lightly-packed glass wool.

The tube is filled with small, amalgamated granules of zinc which should pass a sieve of twenty meshes to the inch, but which should be retained by a 30-sieve. The zinc should contain 1 to 5 per cent. of mercury, which is introduced by shaking the zinc in a large bottle with the necessary volume of a 2 per cent. solution of mercuric chloride acidified with dilute hydrochloric acid. The zinc can be rendered even more active by further shaking with a dilute solution of hydrochloric acid to which a few milligrammes of chloroplatinic acid have been added. After amalgamating, the zinc granules are washed several times with water and are transferred to the reductor. No attempt to pack them tightly should be made, but they may be caused to settle down into their places by tapping gently. They are held in position by a small wad of glass wool. The reductor is then connected up with a filter-bottle as shown. When it is not in use, the zinc should be covered with water and the tube should be stoppered to exclude dust.

The general process of reduction is as follows: If it has been standing idle for some time, the zinc is first activated by drawing through it 100 to 200 ml. of 5 per cent. sulphuric or hydrochloric acid, the choice of the acid being governed by the nature of the titration to be carried out later. The tube should *never* be so far emptied that the top of the zinc column

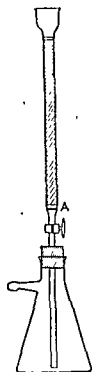


FIG. 81. THE JONES REDUCTOR.

is exposed to the air. After the acid has passed through, it should be followed by 100 ml. of water. These filtrates should be discarded. The reductor is now ready for use.

To reduce a solution of ferric iron, pass through the reductor in succession 50 ml. of 5 per cent. sulphuric acid, 25 ml. of the ferric solution diluted with 100 ml. of the 5 per cent. acid, 50 ml. of the acid, and, finally, 200 ml. of water. The water washes out all the reduced compound and removes acid which would otherwise cause an unnecessary waste of zinc. That part of the 200 ml. of water required to cover the column of zinc should be left in the tube. Before carrying out a determination, a blank to correct for the presence of impurities should always be run, using the same quantities of acid and water as will be used later.

The conditions of use of the reductor are governed by the nature of the substance to be determined, but for salts of iron and other easily-reducible compounds the liquids should be passed through it at speeds of about 100 ml. per minute, at room temperature. If the reduced substance is easily oxidised by the air, an excess of a standard solution of a suitable oxidant can first be placed in the filter-bottle. The solution containing the substance for reduction is then run through the column of zinc straight into the solution of the oxidising agent, the excess of this reagent being titrated at leisure. If it so happens that potassium permanganate is used in the determination and air is allowed to enter the column, a larger volume of permanganate is required than would be the case were air completely excluded. It would therefore appear that air causes the formation of some compound, possibly hydrogen peroxide, which attacks permanganate.

Nitrates, acetates, organic matter in general, and those metals which normally are displaced from solution by zinc, should never be allowed to enter the reductor. A large number of elements, notably iron, chromium, titanium and vanadium, can be reduced in this apparatus, and consequently the reductor is of great value in volumetric analysis.

### Determination of Iron in an Iron Ore

If the iron exists in the ore partly or wholly in the ferric state, the ore is dissolved in acid, the iron is reduced to the ferrous state by one of the methods described above, and is titrated with a solution of potassium dichromate.

Weigh out accurately about 2 gm. of the powdered iron ore. Heat this in a porcelain basin covered by a large funnel (Fig. 35, p. 37) with about 30 ml. of concentrated hydrochloric acid on a hot plate for about half an hour. Dilute the resulting solution slightly with water, allow the undissolved matter to settle, cool, and decant the liquid into a 250-ml. measuring-flask. Heat the undissolved residue again with a small quantity of the acid, which has been diluted with its own volume of water. When it is obvious that all the ore has been decomposed, transfer both the liquid and the residual solid to the flask and make up to the standard volume.

The ferric salt present in one-tenth of this solution is then reduced to the ferrous state by one of the methods described above, and the ferrous iron is titrated. The reduction with stannous chloride and the determination of iron with dichromate, using the external indicator, is recommended. Alternatively, add a measured excess of potassium dichromate to an

## Summary of Methods for the Determination of Iron by Potassium Dichromate or Potassium Permanganate

Method.	Zn Reduction	SO <sub>2</sub> Reduction	SnCl <sub>2</sub> Reduction.	Notes.
$K_2Cr_2O_7$ with $K_2FeC_4N_6$	Interference of zinc with indicator.	Good, but use of $KMnO_4$ is quicker.	Excellent.	
$K_2Cr_2O_7$ with Phenanthroline.	Good.	Good.	Good.	The $K_2Cr_2O_7$ must be added in excess, and this excess must be titrated with standard ferrous solution.
$K_2Cr_2O_7$ with 3a diphenylamine sulphonate.	Fair.	Fair.	Fair.	Presence of phosphoric acid essential.
$KMnO_4$ No indicator.	Excellent.	Good.	In presence of chlorine ions, possible only if phosphoric acid and manganous sulphate are added.	Absence of organic material essential.
$KMnO_4$ with Phenanthroline.	Method Unnecessary.	Method Unnecessary.	Possible in presence of phosphoric acid. Presence of manganous sulphate also desirable.	Absence of organic material essential.

(For use of permanganate solution, see p. 155.)

aliquot portion of the reduced solution and titrate this excess with a standard solution of ferrous iron made by dissolving an accurately-weighed quantity of about 40 gm. of ferrous ammonium sulphate in water, to which dilute sulphuric acid has been added, and diluting to 1 litre. Use ferrous phenanthroline as internal indicator.

If both ferrous iron and ferric iron are present, and each of these is to be determined, the ore must be treated with hydrochloric acid out of contact with the air, as is indicated on p. 142. A portion of the acid solution is used for the determination of the ferrous iron. The ferric iron in the remainder of the solution is reduced to the ferrous state and the total iron is determined with dichromate. The difference between the quantities of iron found by the two titrations gives the amount of ferric iron which was originally present in the ore.

The method described above, while being reasonably reliable, has two disadvantages. First, the presence of the residual solid in the measuring-flask leads to some uncertainty about the real volume of the solution. This is a minor objection. Second, and much more important, it is impossible to examine the solid thoroughly to make sure that all iron has been removed from it. Accordingly, when results of maximum accuracy are desired, the solution must be filtered. Many iron ores contain silica which, on treatment with acid, forms a colloidal solution which it is almost impossible to filter. This silica must be dehydrated, and a somewhat lengthy series of processes is necessary as follows: Digest a weighed quantity of the ore with concentrated hydrochloric acid as before. After half an hour, remove the funnel, having

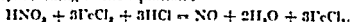
the solution through a filter-paper into the measuring-flask. Add 10 ml. of concentrated hydrochloric acid and 40 ml. of water to the residue, and digest it on the hot plate for a further half hour. Filter into the flask, after cooling, and wash the residue with a small quantity of hot water.

Break the filter-paper and wash the residue back into the dish, using as little water as possible. Add an equal volume of concentrated hydrochloric acid and digest on the hot plate for ten minutes. Place a drop of potassium thiocyanate on a white tile, and add . . . . . appears, continue the . . . . . flask; and so on until a . . . . . last solution and the res . . . . .

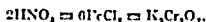
For the determination of iron by potassium permanganate see p. 157; electrometrically, by potassium dichromate, p. 216; and by titanous chloride, p. 185.

### Determination of Nitrates by the Oxidation of a Ferrous Salt

This method is based on the fact that a ferrous salt is quantitatively oxidised by nitric acid in the presence of a considerable excess of hydrochloric acid, according to the equation:



So that



The experiment is carried out as follows: About 0.3 gm. of the nitrate ( $\text{KNO}_3$  is suitable for practice) is accurately weighed and is dissolved in a little water in a 200-ml. distillation-flask fitted with a side-tube. The neck of the flask is closed by a rubber bung, which carries a dropping-funnel and an inlet tube reaching well down inside the flask. The flask is placed in an inclined position,

A brisk stream of  $\text{CO}_2$  from a Kipps' apparatus is now passed through the inlet tube to displace all air. When the air has been displaced, the rate of passage of the  $\text{CO}_2$  is very much reduced, and a measured excess of an arbitrary solution of ferrous sulphate is added through the dropping-funnel. Fifty millilitres of a solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , containing 140 gm. of the salt and a little sulphuric acid per litre of solution, will probably be suitable.

Some 40 ml. of pure, concentrated  $\text{HCl}$  are added, and any ferrous salt remaining in the funnel is washed into the flask, using as little water as possible. The contents of the distillation-flask are gently boiled. The colour of the solution at first will be dark, almost black, and boiling must be continued for at least five minutes after the colour of the ferric chloride has appeared. A slow stream of  $\text{CO}_2$  must be kept passing through the apparatus.

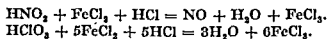
During the reduction of the nitrate, a considerable quantity of  $\text{HCl}$  gas will be distilled over. These fumes may be absorbed in water by attaching one end of a 50-ml. pipette to the side-tube of the distillation-flask and dipping the other end of the pipette beneath the surface of a little water in a beaker. After the action is over, the  $\text{CO}_2$  is passed through the apparatus until the solution is cold, and the solution is diluted and titrated with seminormal  $\text{K}_2\text{Cr}_2\text{O}_7$ ; 25 ml. of the arbitrary solution of ferrous sulphate are then titrated against the dichromate.

As it is almost impossible to prevent oxidation of the ferrous chloride by some substance other than the nitrate, a better plan is to carry out a check experiment at the same time as the oxidation, using similar apparatus and manipulation, the only difference being that in the check the nitrate is absent. If 50 ml. of the ferrous sulphate solution are used for the check, the difference between the two titrations will give the weight of nitrate directly in terms of the standard dichromate; it is not necessary to calculate the concentration of the ferrous solution.

A more convenient procedure is to use titanous chloride to determine the ferric iron produced by the oxidation (p. 187).

### Determination of Nitrites and Chlorates

Nitrites and chlorates can be determined by the ferrous salt method described above, the procedure being similar to that described for nitrates. The equations are:

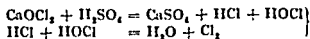


As chloric acid is a better oxidising agent than nitric acid, the oxidation with the former acid proceeds quantitatively in the presence of  $\text{H}_2\text{SO}_4$ . It is therefore better to use this acid in place of  $\text{HCl}$ , because ferrous sulphate is much less rapidly oxidised by the oxygen of the air than is ferrous chloride.

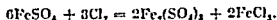
### Evaluation of Bleaching-powder and the Determination of Hypochlorites by the Oxidation of a Ferrous Salt

Bleaching-powder is a substance containing calcium, chlorine and oxygen. It is made by passing chlorine over slaked lime, and its

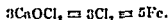
composition can be represented by the formula  $\text{CaOCl}_2$ . On treatment with an acid, it is decomposed with the evolution of chlorine :



If a ferrous salt is present when the acid is added, the chlorine immediately oxidises this salt.



Whence



That is, one atom of iron is oxidised by every "available" chlorine atom in the bleaching-powder.

It is found convenient in practice to add the "solution" of bleaching-powder to an excess of an acidified solution of a ferrous salt, and then to determine the amount of unchanged salt by means of dichromate solution.

**The Standard Solution of Ferrous Salt.** A solution containing 4 grm. of iron per litre will be found suitable. The solution is prepared by dissolving the proper quantity of ferrous ammonium sulphate (p. 140) in water acidified with dilute sulphuric acid.

**Preparation of the Bleaching-powder Liquid.** The solution is prepared from 10 grm. of the bleaching-powder and is made up to 1 litre according to the following directions: Weigh out the bleaching-powder from a stoppered weighing-tube. As bleaching-powder is attacked by the moisture in the air, with evolution of chlorine, it is essential, in order to prevent damage to the balance, that the powder be kept covered during weighing. Place the powder in a smooth porcelain mortar, preferably one which is glazed inside, and add a few millilitres of water. Rub the mixture into a paste by means of the pestle, and add more water and continue the rubbing until a thin cream is formed. Allow the solid to subside and decant the liquid into a litre flask.

Then triturate the residue repeatedly with fresh quantities of water, stirring up the liquid and pouring it off after each treatment, until the whole of the solid has been transferred to the flask. Finally, fill up the flask to the mark with water, and mix its contents well by shaking. The liquid will always be milky, because bleaching-powder is not completely soluble in water. The solution must be titrated at once, because it undergoes rapid change, and the flask should be shaken immediately before each aliquot portion is withdrawn.

**The Process of Titration.** Take 50 ml. of the iron solution in a conical flask and acidify it further by adding 10 ml. of dilute sulphuric acid. Add 25 ml. of the freshly-shaken bleaching-powder suspension, mix the liquids well, and determine the weight of residual ferrous iron by means of standard potassium dichromate solution. The difference between this weight and the weight of iron in the 50 ml. originally taken will give the weight of ferrous iron which has been oxidised by the bleaching-powder solution.

The Following Example is a record of the results which were obtained in a determination, together with the calculation of the percentage of available chlorine present in the bleaching-powder :

10 grm. of bleaching-powder were treated with water and the liquid was made up to 1 litre.

25 ml. of this liquid converted 0.1208 grm. of ferrous iron into the ferric state. According to the equation and statement on p. 153, this indicates the presence of

$$\frac{0.1208 \times 85.46}{55.84} = 0.0767 \text{ grm.}$$

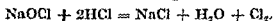
of Cl in 25 ml. of bleaching-powder liquid.

Now 25 ml. of the bleaching-liquid corresponds with 0.25 grm. of bleaching-powder ; therefore the percentage weight of available chlorine

$$= \frac{0.0767 \times 100}{0.25} = 30.7.$$

Other Methods for determining the available chlorine in bleaching-powder are given on pp. 170 and 184.

**Determination of Hypochlorites.** The determination of a hypochlorite, such as sodium hypochlorite, is carried out on exactly the same lines as that of available chlorine in bleaching-powder. One molecule of sodium hypochlorite, however, oxidises two atoms of iron :



Whence

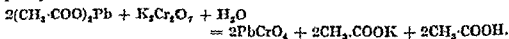


### Determination of Lead

Two dichromate methods are available. In the first, the lead is precipitated from an acetic acid solution by an excess of potassium dichromate, the precipitate is removed by filtration, and the excess of potassium dichromate determined with a standard solution of ferrous ammonium sulphate. In the second, an equivalent quantity of the dichromate is added to the lead solution, the end-point being determined with silver nitrate as an external indicator.

Weight out accurately that quantity of material which is thought to contain about 0.25 grm. of lead. Dissolve it in 10 ml. of 50 per cent. nitric acid. Neutralise the excess of nitric acid with ammonia.

**Method I.** Dissolve any precipitate in acetic acid and add sodium acetate. Add a known volume, in excess, of a standard solution of potassium dichromate containing approximately 5 grm. of the salt per litre. Note that the dichromate is being used, not as an oxidant, but as a precipitant :



Hence 414.4 grm. of lead are precipitated by 294.2 grm. of dichromate. Thus 50 ml. of the solution should be more than sufficient to precipitate all the lead originally taken.

Boil for at least two minutes, filter off the precipitate, using a Gooch crucible, wash with a hot solution of sodium acetate prepared by diluting 5 ml. of a cold, saturated solution of that salt with 100 ml. of water.

Finally, titrate the excess of dichromate with a decinormal solution of ferrous ammonium sulphate, using either potassium ferrieyanide as external indicator or ferrous phenanthroline as internal indicator.

*Method II.* Add a considerable excess of acetic acid to the solution of lead in nitric acid, which has been neutralised with ammonia. Boil, and add, from a burette, a standard solution of potassium dichromate containing 7 to 8 grm. of the salt per litre in quantity sufficient to precipitate nearly all the lead. Boil until the colour of the precipitate is orange, and finish the titration, using a 3 per cent. solution of silver nitrate as external indicator.

Reliable results will be obtained by this method only if (a) the solution of lead is concentrated; (b) it is kept as hot as possible; (c) the concentrations both of the dichromate and of the indicator are near to those given above.

A method for the determination of lead chromate iodometrically is given on p. 173.

## USE OF POTASSIUM PERMANGANATE SOLUTION

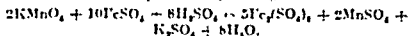
**Introductory Remarks.** Potassium permanganate solution, provided the conditions are suitable, readily yields a definite portion of its oxygen to certain readily oxidisable substances, and may therefore be used instead of potassium dichromate solution for many volumetric determinations. It presents the advantage over dichromate that it becomes colourless when it is reduced: an indicator is therefore unnecessary, since the presence of the slightest excess of permanganate is indicated by its colour. It possesses the further advantage that it is a stronger oxidising agent than dichromate.

The false belief is current that permanganate cannot be used in the presence of hydrochloric acid, but it is only when hydrochloric acid is present together with iron or certain other catalysts that the results are unsatisfactory. It is possible, for example, to determine with great accuracy the percentage of calcium oxalate in a sample of that salt by making a solution in hydrochloric acid and titrating with permanganate. However, because of the possible accidental presence of a trace of iron or other active impurity, a liquid which is to be titrated with permanganate should preferably be acidified with dilute sulphuric acid. Nitric acid must not be present in any quantity.

When a solution of potassium permanganate is exposed to light, it gradually becomes more dilute by the decomposition of the salt. The solution must therefore be kept in a dark-blue Winchester quart bottle and stored in a cool and dark place. Owing to this liability to change, the permanganate solution should be standardised not only immediately after its preparation, but also at frequent intervals.

## Preparation, Standardisation, and Use of Potassium Permanganate Solution

The following reaction takes place when a cold, acidified solution of ferrous salt is titrated with potassium permanganate:





It will be seen from the equation that two molecules of  $\text{KMnO}_4$  oxidise ten atoms of ferrous iron. Now, as two atoms of iron are oxidised by one atom of oxygen ( $4\text{FeO} + \text{O}_2 = 2\text{Fe}_2\text{O}_3$ ), two molecules of  $\text{KMnO}_4$  must contain five atoms of oxygen available for oxidation. A decinormal solution will therefore contain

$$\frac{158.03 \times 2}{10 \times 10} = 3.161 \text{ grm. of the crystals.}$$

It is convenient to remember that 3 grm. of  $\text{KMnO}_4$  are approximately equivalent to 5 grm. of  $\text{K}_2\text{Cr}_2\text{O}_7$  and will oxidise nearly 5.6 grm. of iron. Accordingly, to make an approximately decinormal solution weigh out 3 grm. of potassium permanganate crystals, dissolve them in water in a litre flask, and dilute to 1 litre with water. Potassium permanganate dissolves slowly in cold water and, as it should not be heated, it is essential that the crystals be ground finely. Great care must be taken that all the reagent has dissolved before any of the solution is used.

The ferrous sulphate solution should be made, preferably using ferrous ammonium sulphate, immediately before it is required for the titration; it contains approximately 40 grm. of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  per litre, and the presence of a considerable quantity of dilute sulphuric acid to prevent hydrolysis is essential. Better, weigh out accurately portions of about 1 grm. of the salt, and dissolve them separately in dilute sulphuric acid. Each portion will be equivalent to approximately 25 ml. of the permanganate.

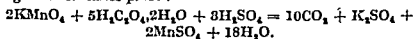
The subsequent procedure is similar to that already described under the standardisation of potassium dichromate; the use of an indicator, however, is unnecessary, since the end of the reaction is marked by the appearance of a pink tint in the liquid, caused by the presence of a small excess of the strongly-coloured permanganate.

Pour some of the permanganate solution into a burette fitted with a glass stop-cock, filling the burette to the zero mark. Read from the top of the meniscus, because the liquid is strongly coloured. Allow the permanganate solution to flow into the cold ferrous solution, which has been acidified with about 10 ml. of dilute sulphuric acid, and has been diluted with distilled water.

Continue the addition of the permanganate solution until a faint permanent pink colour remains after the liquids have been mixed. This colour is readily seen when the beaker containing the solution of iron is placed on a piece of white paper, or on a white tile.

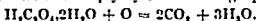
Two titrations should be made, and they must not differ from one another by more than 0.1 ml.

**Standardisation of Potassium Permanganate Solution by means of Oxalic Acid.** When potassium permanganate solution is added to a warm solution of oxalic acid which has been acidified with sulphuric acid, the following reaction takes place:



It will be seen, on comparing this equation with that given for a ferrous salt, that 126.1 grm. of crystalline oxalic acid are equivalent to 117.7 grm. of iron, and require 16 grm. of oxygen for their complete oxidation. This

is provided by  $\frac{2\text{KMnO}_4}{5}$ , or 63.2 gm. of permanganate. The oxidation of oxalic acid is shown more simply by the following equation :



A Standard Solution of pure recrystallised oxalic acid, of approximately decinormal concentration, is required for the titration. This is prepared by dissolving an accurately-weighed quantity of about 1.5 gm. of the pure crystals in water, and by diluting the solution to 250 ml. To 50 ml. of this solution in a conical flask, add 10 ml. of dilute sulphuric acid, dilute considerably with water, heat to 60° C., and run in the solution of potassium permanganate, containing about 3 gm. per litre, until a faint permanent pink tint remains in the liquid after it has been mixed. If the permanganate is added too rapidly, a brown precipitate forms, which is removed with difficulty by adding more sulphuric acid. In this event traces of oxygen will be evolved, and the result may be low.

*Note.* In work where the most accurate results possible must be obtained, potassium oxalate is substituted for the standard. This should be carefully

On the other hand, samples of permanganate of high purity can now be obtained, and it is sometimes sufficiently accurate to make up a standard solution of this reagent by weighing. A solution standardised by weighing must be used immediately.

### Determination of Iron by means of Standard Permanganate

The iron present in a substance in the ferrous or the ferric condition, or partly in each condition, may be determined by titration with standard permanganate solution, instead of by dichromate, if oxidisable organic matter and hydrochloric acid are absent. The method is similar to that described for potassium dichromate, except that the use of a special indicator is unnecessary (see pp. 145 and 150).

When using permanganate, it is advisable to reduce ferric iron with zinc and sulphuric acid or with sulphur dioxide, and not with stannous chloride, and to avoid altogether the use of hydrochloric acid. The ferric ion acts as a catalyst and in its presence potassium permanganate will slowly oxidise hydrochloric acid. This means that a sharp end-point cannot be obtained, because the pink colour is continually fading.

On the rare occasions when the use of potassium permanganate for the determination of iron in the presence of hydrochloric acid proves unavoidable, reasonably accurate results can be obtained by carrying out the titration in

Introduction of 2 drops of ferrous phenanthroline indicator (p. 145).

### Determination of Oxalate in Solution by means of Standard Permanganate

An oxalate which is soluble in water, or in dilute mineral acids, is readily determined by means of standard permanganate solution. About 2.5 gm.

of the oxalate are accurately weighed and dissolved in water, or in dilute acid, and the solution is made up to 250 ml. The subsequent titration follows closely the method used for standardising a solution of permanganate with oxalic acid (p. 156).

**Determination of Ferrous Oxalate.** A suitable quantity of the salt is weighed out into a beaker and dissolved in a small quantity of warm, dilute  $\text{H}_2\text{SO}_4$ . The solution is cooled, transferred to a measuring-flask, and made up to a known volume.

An aliquot portion is taken, diluted, further acidified with  $\text{H}_2\text{SO}_4$ , and titrated warm with potassium permanganate. The volume of the  $\text{KMnO}_4$  used is a measure of  $\text{Fe} + \overline{\text{C}_2\text{O}_4}$ .

The iron in the aliquot portion, after the destruction of the oxalate radical, is reduced with zinc and sulphuric acid, the unused zinc is removed (p. 147), and the ferrous iron is again oxidised with the standard  $\text{KMnO}_4$ . The volume of permanganate now used is a measure of the iron only, and the oxalate can be determined by difference.

It is impossible to determine the iron alone by titrating first of all in the cold, because some of the oxalate radical is inevitably oxidised; the manganese sulphate produced in the reduction of the permanganate by the iron acts as a catalyst.

#### Determination of Calcium in Solution by means of Standard Permanganate

The calcium is precipitated by adding a measured volume of standard oxalic acid solution in excess. Either the excess of oxalic acid is then determined by titration with standard potassium permanganate solution; or, better, the oxalate radical present in the calcium oxalate precipitate is determined (compare p. 156).

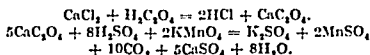
**Procedure.** Add to the boiling solution of the calcium compound, contained in a flask, ammonium hydroxide solution in excess, and a measured volume of standard oxalic acid solution, in quantity more than sufficient to precipitate all the calcium as oxalate. Allow the precipitate to settle and then decant the hot liquid through a filter-paper, finally transferring the precipitate to the paper. Wash with hot water, to which a little ammonia has been added, until a few drops of the runnings when warmed in a test-tube with dilute  $\text{H}_2\text{SO}_4$  and very dilute permanganate solution fail to decolorise the latter.

Then, either acidify the filtrate with dilute  $\text{H}_2\text{SO}_4$ , heat it to  $60^\circ \text{C.}$ , and titrate the excess of oxalic acid with a standard solution of potassium permanganate;

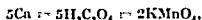
Or dissolve the clean precipitate of calcium oxalate by pouring hot, dilute  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  over the filter-paper. If  $\text{H}_2\text{SO}_4$  is used, a persistent white residue may be left on the paper. Neglect this, as it will only be calcium sulphate, provided that the paper has been washed three or four times with acid. Titrate the filtrate and washings with standard permanganate as described above. If this second method is adopted it is better to precipitate the calcium oxalate as follows: Acidify the solution of calcium with hydrochloric acid and add a solution of ammonium oxalate

in excess. Boil, and precipitate the calcium oxalate by adding ammonium hydroxide in excess to the boiling solution.

The equations are :



Hence



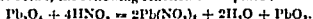
or  $5 \times 40.1$  grm. of calcium are equivalent to  $316.1$  grm. of  $\text{KMnO}_4$ .

**Determination of Other Metals by Standard Permanganate.** Any metal which gives an insoluble oxalate can be determined by the method described above. Lead is such a metal. It is precipitated as oxalate by adding oxalic acid to a solution of lead which has been made strongly acid with acetic acid. In this case it is better to determine the excess of oxalic acid in the filtrate, but the washed precipitate of lead oxalate may be dissolved in dilute nitric acid (which has been boiled to expel traces of nitrous acid); or it may be decomposed with dilute sulphuric acid and the amount of oxalate radical equivalent to the lead determined in the resulting solution.

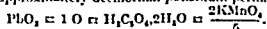
For the determination of Bismuth by this method, consult the 12th Edition of *Sutton's Volumetric Analysis*.

#### Determination of Dioxides by Potassium Permanganate

**Lead Dioxide** in a sample of that compound, or in **Red Lead**. Weigh out accurately about  $0.3$  grm. of the substance into a conical flask and add  $30$  ml. of  $10$  per cent. nitric acid, which must be free from nitrous acid, and heat. In the case of the red lead, the following reaction takes place :



When the reaction is over, add  $50$  ml. of a standard solution of oxalic acid of approximately decinormal concentration, heat nearly to boiling, and titrate hot with standard, approximately decinormal potassium permanganate solution.

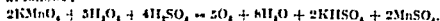


For the determination of manganese dioxide by this method, see p. 267.

#### Determination of Hydrogen Peroxide by Potassium Permanganate

Commercial hydrogen peroxide is sold in three concentrations, containing  $5$ ,  $10$  or  $20$  times its own volume of "available" oxygen. The so-called " $10$ -volume" solution should provide ten times its own volume of oxygen, measured at  $0^\circ \text{C}$ . and  $760$  mm., and should contain  $3.01$  per cent. of  $\text{H}_2\text{O}_2$ , or  $1.43$  per cent. by weight of "available" oxygen.

place as follows :



**Procedure.** Take a measured volume of the solution of hydrogen peroxide ( $25$  ml. of the  $10$  volume reagent will be suitable) in a  $250$ -ml. measuring flask and dilute to the mark with water, which must itself have no appreciable reaction with acidified potassium permanganate.

Add  $5$  ml. of dilute sulphuric acid to about  $500$  ml. of water in a porcelain dish, and add decinormal permanganate solution until a faint permanent pink colour persists. Read the burette. Add  $25$  ml. of the diluted hydrogen peroxide solution, and continue the addition of the permanganate until the faint pink colour again becomes permanent. The difference between the two burette readings is a measure of the hydrogen peroxide present. The proportion of hydrogen peroxide found in the solution can be expressed either as percentage of peroxide by weight, or as percentage of "available" oxygen by volume.

Oxidisable organic compounds, such as glycerol, are sometimes added to a solution of hydrogen peroxide to preserve it. Their presence can be detected by determining the  $\text{H}_2\text{O}_2$  by the above process and also gasometrically (p. 267) or iodometrically (p. 179). If the first method gives the higher result, some such impurity is probably present.

#### Determination of Nitrites by Standard Permanganate

Nitrous acid is oxidised by potassium permanganate according to the equation  

$$2\text{KMnO}_4 + 5\text{HNO}_2 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{HNO}_3 + 3\text{H}_2\text{O}.$$
 The reaction proceeds readily only if the solution is warm, but low results may be obtained if the acid is not sufficiently strong.

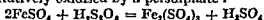
This is diluted with water, acidified with sulphuric acid, and warmed to about  $40^\circ\text{C}$ . The solution of the nitrite to be analysed is then run in from a burette. If the end-point is approached slowly and the liquid is constantly stirred, excellent results are obtained.

(b) A measured excess of the standard permanganate is placed in the flask, diluted with water, and acidified with sulphuric acid. A known volume of the nitrite is then added, the solution is heated to  $60^\circ\text{C}$ ., and the excess of permanganate is determined by titration with standard oxalic acid.

In these, as in nearly all other oxidation-reduction reactions, it is advisable to use solutions not stronger than decinormal.

#### Determination of Persulphates by Standard Permanganate

This method is based on the fact that an acidified solution of a ferrous salt is easily and quantitatively oxidised by a persulphate :



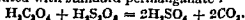
The excess of ferrous salt is determined by standard permanganate.

The method is similar to the determination of a nitrate by the ferrous salt method, using potassium dicromate (p. 152). However, as ferrous sulphate is not so easily oxidised by atmospheric oxygen as ferric chloride, elaborate precautions against accidental oxidation are unnecessary.

The persulphate to be analysed is weighed out into a flask and a measured excess of an arbitrary ferrous sulphate solution is added. Then 200 ml. of hot water are added and the solution is allowed to stand. Reduction will be complete in about one minute after the salt has dissolved, provided the temperature is above  $80^\circ\text{C}$ . For lower temperatures allow longer times. As the persulphate may be decomposed by hot water, the ferrous sulphate should be added before the water. The excess of ferrous sulphate is titrated with standard permanganate, the ferrous sulphate solution being standardised against the permanganate under the same conditions.

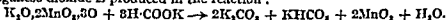
**Determination of Persulphates with Oxalic Acid.** Persulphates do not ordinarily react with oxalic acid, but in a boiling solution in the presence of a catalyst, conveniently silver sulphate, the oxidation is rapid and complete.

The persulphate is weighed out into a large conical flask, and a measured excess of a standard solution of oxalic acid, together with about 10 ml. of a 10 per cent. solution of sulphuric acid saturated with silver sulphate, are added. The solution is heated on a water-bath until the evolution of  $\text{CO}_2$  has ceased. This may require about twenty minutes. The solution is then diluted, warmed if necessary, and titrated with standard permanganate :



#### Determination of Formic Acid and Formates by Standard Permanganate

Formic acid reacts only slowly in the cold with an acidified solution of potassium permanganate. If the solution is hot, some of the acid is lost by volatilisation. On the other hand, a formate is easily oxidised by potassium permanganate in the presence of a strong base, but as only three of the oxygen atoms in the double permanganate molecule are available for oxidation, manganese dioxide is produced in the reaction :



The presence of the precipitated manganese dioxide makes the recognition of the end-point difficult. It is therefore better to add first an excess of per-

mannic acid carrying manganese dioxide in suspension.

For practice, take 25 ml. of a solution containing 3 grm. of sodium formate per litre and add a considerable excess of sodium carbonate. Heat the solution to 60° C., and add to it, from a burette, about 25 ml. of a 0.1 N. solution of permanganate until the presence of an excess of this reagent is marked by the appearance of a definite and persistent red colour. Add an excess of a standard

**Calculation.** At the final end-point the solution is acid, and, as the final products of a chemical reaction are independent of the stages by which that reaction has been brought to completion, five atoms of oxygen per double molecule of permanganate have been used. Therefore ignore the equation given above save to note that one molecule of sodium formate requires one atom of oxygen for its complete oxidation. In an actual determination the following results were obtained:

To 25 ml. of a solution containing 3 grm. of a sample of sodium formate per litre were added 25 ml. of 0.1 N.  $\text{KMnO}_4$ . After the reaction in alkaline solution was completed, 20 ml. of 0.1 N. oxalic solution were added. After the addition of dilute sulphuric acid, 12.3 ml. of the  $\text{KMnO}_4$  were required to reach the end-point. Because both solutions were decinormal:

*Oxidising Agents.*

*Reducing Agents.*

$$(25 + 12.3) = 37.3 \text{ ml. } \text{KMnO}_4 \equiv 25 \text{ ml. H-COONa} + 20 \text{ ml. H}_2\text{C}_2\text{O}_4.$$

$$20 \text{ ml. } \text{KMnO}_4 \equiv 20 \text{ ml. H}_2\text{C}_2\text{O}_4.$$

Therefore,  $(37.3 - 20) = 17.3 \text{ ml. } \text{KMnO}_4 \equiv 25 \text{ ml. H-COONa}.$

Now  $2\text{KMnO}_4 \equiv 5\text{O} \equiv 5\text{ H-COONa}$

or  $316 \text{ grm. } \text{KMnO}_4 \equiv 5 \times 68 \text{ grm. H-COONa}.$

$$\therefore \frac{17.3 \times 316}{1000} \text{ grm. } \text{KMnO}_4 \equiv \frac{5 \times 68 \times 17.3 \times 3.16}{1000 \times 316} \text{ grm. H-COONa}.$$

This quantity of formate was in 25 ml. of solution.

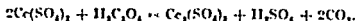
$$\text{Hence the weight of formate per litre} = \frac{5 \times 68 \times 17.3 \times 3.16 \times 1000}{1000 \times 316 \times 25} \text{ grm.} \\ = 2.35 \text{ grm.}$$

Therefore the percentage of sodium formate in the sample was

$$\frac{2.35 \times 100}{3} = 78.3.$$

### USE OF CERIC SULPHATE SOLUTION

The oxidising power of ceric sulphate is comparable with that of potassium permanganate, but it has the great advantage that its reduction is a one-stage process:



Therefore it can be used without paying that strict attention, which is sometimes necessary in the case of permanganate, to the working conditions under which a determination is made. Further, it will not readily oxidise hydrochloric acid in the presence of iron, and its solution is more stable than that of permanganate. On the other hand, as its natural

yellow colour is much less pronounced than is the purple colour of permanganate, the end-points are much more difficult to detect when colourless solutions are being titrated, and the use of some auxiliary indicator becomes essential when the solutions are coloured. This reagent, however, is particularly suited to use with the electrometric method (pp. 214-220).

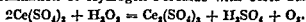
### Preparation and Standardisation of Ceric Sulphate Solution

The molecular weight of ceric sulphate is 332.2. It will be seen from the above equation that two molecules provide one atom of "available" oxygen, and hence the equivalent weight is also 332.2 and a decinormal solution will contain 33.22 gm. of the salt per litre. It is customary in ordinary work to use a 0.05 to 0.1 N. solution.

The ceric sulphate ordinarily purchased contains only about 50 per cent. of the salt. Therefore weigh out approximately 60 to 70 gm. of the finely-powdered material. Digest this for three or four hours with hot, dilute sulphuric acid, adding more acid from time to time as seems necessary. Cool. Decant the solution through a filter-paper and dilute to 1 litre.

Standardise this solution against oxalic acid or sodium oxalate, following the method given for the standardisation of permanganate (p. 156). The solution to be titrated must be diluted to 200 ml. and contain about 15 ml. of concentrated hydrochloric acid or 40 ml. of 10 per cent. sulphuric acid. Titrate at 70° C. until the colour of the solution becomes faintly yellow.

### Determination of Hydrogen Peroxide with Ceric Sulphate



The method for obtaining a suitable weight of hydrogen peroxide for analysis is given on p. 159. To a suitable volume of the solution of hydrogen peroxide in a conical flask, add 10 ml. of dilute sulphuric acid and a few lumps of ice. Dilute to 200 ml. and titrate with the standard ceric sulphate solution, using either the colour of the reagent itself or ferrous phenanthroline as indicator.

### Determination of Ferrous Iron with Ceric Sulphate

To the solution, which should contain about 0.15 gm. of iron in 150 to 200 ml., add 25 ml. of a mixture containing 150 ml. of concentrated sulphuric acid, and 150 ml. of concentrated phosphoric acid per litre. Titrate with standard, approximately decinormal ceric sulphate solution, using either ferrous phenanthroline or xylene cyanol FF as indicator. The reduced form of this latter indicator is green; the oxidised form is red. Ten drops of a 0.1 per cent. aqueous solution should be used.

The reaction proceeds equally well with either indicator if the ferrous solution is added to the solution of ceric sulphate.

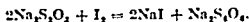
results are unreliable.

### USE OF STANDARD SOLUTIONS OF IODINE AND SODIUM THIOSULPHATE

Iodine, dissolved in an aqueous solution of potassium iodide, can be used as an oxidising agent in many different reactions. As, however, it does not always react quickly, it is more usual to add the standard iodine

solution in excess, and to determine the excess with a solution of sodium thiosulphate. Therefore the two solutions are nearly always used in association.

Sodium thiosulphate reacts with iodine to give sodium iodide and sodium tetrathionate :



Of these reagents, only iodine is coloured, and therefore it should be possible to judge the end-point by the disappearance of the faint yellow colour of a dilute aqueous solution of iodine. This method is in fact sometimes used. The end-point, however, is made much more obvious by the addition of starch solution, which gives an intense blue colour in the presence of a small quantity of iodine. This colour may be a dirty brown if much iodine is present and, therefore, titrations should be carried as far as possible without the starch, this indicator being added within 2 to 3 drops of the end-point.

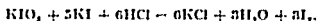
### Preparation and Standardisation of the Solutions

It is customary to use approximately decinormal solutions of iodine and sodium thiosulphate.

**Preparation of a Solution of Iodine.** As the equivalent weight of iodine is 126.92, a decinormal solution contains 12.692 grm. of the element per litre.

Weigh out about 13 grm. of pure iodine into a litre flask from a stoppered bottle, taking care to remove the bottle from the balance-case before taking out the stopper. Then add about 20 grm. of pure potassium iodide and about 40 ml. of water. Shake the contents of the flask until complete solution has taken place, adding more of the iodide, if necessary, to complete the solution of the iodine. Then fill the flask up to the mark with distilled water. The solution must be kept in a well-stoppered bottle, and in a cool, dark place.

*Alternatively*, as a solution of iodine must be re-standardised frequently, a solution containing potassium iodate and potassium iodide can often be used in its stead in many determinations. This solution does not deteriorate if it is kept in a stoppered bottle, and a known weight of iodine can be obtained from it when required, by the addition of acid to a suitable volume of it. As very pure potassium iodate is obtainable, a standard solution can be made by dissolving a known weight of this salt in water and by diluting the solution suitably. On the addition of an acid, potassium iodate oxidises the iodide quantitatively, according to the equation :



Thus, one molecule of iodate, of molecular weight 214.02, produces six atoms of iodine. To make 1 litre of a decinormal solution, weigh out 3.567 grm. of potassium iodate. Dissolve the salt in about 100 ml. of hot water (it dissolves very slowly in the cold), cool, transfer to a litre flask, add 20 grm. of potassium iodide (excess), and make up to 1 litre with distilled water. If 25 ml. of this solution are taken and acidified with 3 to 4 ml. of normal hydrochloric acid, iodine exactly equivalent



## 22. PREPARATION OF OXIDATION AND REDUCTION

with sodium thiosulphate in 20 ml. of a decinormal solution of that salt with the standard.

**Preparation of a Solution of Sodium Thiosulphate.** As two molecules of crystalline sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , are equivalent to two molecules of iodine a decinormal solution contains 24.85 gram of the crystals per litre. Weigh out about 25 gram of the salt, having crushed the crystals if necessary. Dissolve in water and make up to 1 litre in a volumetric flask.

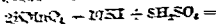
A standard solution of sodium thiosulphate cannot be made up accurately by direct weighing, because the crystals usually supplied are of indeterminate composition. In calculations involving sodium thiosulphate an advantage is therefore to be gained by considering the crystalline salt, and it is conventional to express results in terms of the anhydrous salt (molecular weight, 158.1). All solutions of sodium thiosulphate must therefore be standardised against some standard substance and, as they undergo change on storage, they must be re-standardised from time to time. They should be kept in dark-brown Winkler-type bottles in a cool, closed cupboard. The rate of decomposition is lessened considerably by adding 0.2 gram of sodium carbonate and 100 ml. of chloroform to each litre of the solution.

**Preparation of the Starch Solution.** Make about 1 gram of "soluble starch" into a thin cream by grinding it in a mortar with a small quantity of cold water. Pour this into about 100 ml. of boiling water, and continue to boil for one minute. Allow the liquid to cool, and pour off the clear solution through a folded filter paper. Use up to 5 drops in each titration. This solution does not give an intense colour with iodine after it has been kept for some time, although if it is shaken with a few drops of chloroform directly after it is made, its active life is prolonged.

**Standardisation of the Iodine and Thiosulphate Solutions.** It is generally necessary to standardise only one of these solutions and then to determine the value of the other solution in terms of it.

The thiosulphate solution is best standardised against a solution of iodine made from potassium iodate (p. 163).

It can also be standardised against a solution of about 0.5 gram of potassium dichromate, and dilute to 200 ml. Add a little acid, and at once run in from a 20 ml. of standard approximately. The following reaction takes place

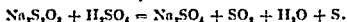


Potassium dichromate with the sodium iodide. Add 4 or 5 ml. of dilute sulphuric acid. If a solution of sodium thiosulphate has been used. It is in a stoppered bottle, so that as the solution is added so as to not otherwise absorb iodine.

little  
of

or

The hydrogen iodide produced by the action of the sulphuric on the potassium iodide may be oxidised by the air and give high results. This danger is minimised by using only a small quantity of potassium iodide and a very small excess of sulphuric acid. A large excess of sulphuric acid will also attack the thiosulphate as follows:—



The thiosulphate solution can also be standardised against potassium dichromate. This is less satisfactory. The green colour of the chromium salt does not mask the end-point with starch, but the dichromate does not oxidise hydriodic acid at all readily. Some five minutes must be allowed to elapse between the addition of the oxidising agent and the titration. During this time the excess of hydriodic acid may be oxidised by the air. The bare minimum of sulphuric acid must therefore be used. It is best to allow the reagents to react in fairly concentrated solution in a stoppered flask and, after five minutes, to dilute to 500 ml. before titration.

It is obvious that if a standard solution of sodium thiosulphate is available, iodates, permanganates and dichromates may be determined by the methods described above.

An Iodine Solution may be standardised very accurately either against a known weight of pure barium thiosulphate crystals,  $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; against a freshly-standardised solution of sodium thiosulphate; or against pure arsenious oxide (p. 160).

If barium thiosulphate is used, weigh out accurately 0.5 to 0.6 gm. of the pure crystals into a conical flask. Add water, and, without waiting for the crystals to dissolve, run in the iodine slowly from a burette. The solution should never be more than faintly coloured by the iodine. When only a small quantity of solid barium thiosulphate remains, add starch and complete the titration slowly.



### Determination of Tin in Solution by Iodine

When an iodine solution is brought into contact with a stannous chloride solution, one molecule of iodine ( $\text{I}_2$ ) converts one molecule of stannous chloride ( $\text{SnCl}_2$ ) into the stannic compound.

Weigh out accurately about 1.5 gm. of tin, or an equivalent weight of a tin salt. Dissolve the metal in 25 ml. of hydrochloric acid diluted with its own volume of water; this operation may be hastened by adding a few drops of chloroplatinic acid, but, if the solution is boiled, or heated nearly to boiling, some of the tin may be lost by volatilisation. Make up the solution to 250 ml., filtering if necessary. As some of the tin will have been oxidised during this process, the metal must be completely reduced as follows:

A conical flask of 500 ml. capacity is closed by a cork, which is fitted with a Bunsen valve, and which also carries a long glass rod, flattened into a disc at one end and reaching nearly to the bottom of the flask. A strip of nickel foil some 4 inches long, 1 inch wide, and 0.01 inch thick is wound round the rod and supported by the disc.

Transfer 25 ml. of the tin solution to the flask, and dilute it with concentrated hydrochloric acid and sufficient water to produce about

40 per cent. hydrochloric acid. Activate the nickel by dipping it into a hot, concentrated solution of ferric chloride in hydrochloric acid for two minutes. Wash it, and place it in the tin solution. Heat the flask on the hot plate until hydrogen is evolved freely, but do not boil the solution or stannic chloride will be volatilised and lost. The brisk evolution of hydrogen is maintained for at least forty minutes. The hydrogen will escape through the Bunsen valve.

When the reduction is judged to be complete, slip off the valve-rubber from its short piece of glass tubing and connect up a Kipp's carbon dioxide apparatus to the glass tubing. Care must be taken to eliminate air by first flushing out all tubing and wash-bottles with a stream of carbon dioxide. At the same time, take the flask from the hot plate and remove the nickel from contact with the solution by pulling up the glass rod through the cork for the necessary distance. The cork must not be taken out. Cool the flask under the tap. The entry of air must be prevented by maintaining the atmosphere of carbon dioxide at the slightly positive pressure made possible by the use of Kipp's apparatus, as the solution of tin is very easily oxidised. When it is quite cold, remove the fittings, wash down the nickel with cold, distilled water (from which all air has been removed) and titrate at once with a standard solution of iodine, adding starch as the end-point is approached.

Note that if the determination is unsatisfactory, the tin is not irremediably lost. The nickel foil can be replaced and the reduction repeated, though in this case it will probably be necessary to add a further quantity of hydrochloric acid to maintain the concentration.

Alternatively, the tin may be reduced with aluminium foil, or, better, with precipitated antimony. The latter metal need not be completely dissolved by the hydrochloric acid before the titration, because it will react only very slowly with the cold solution. Add 50 ml. of concentrated hydrochloric acid to the tin solution, dilute to 200 ml. and add 1 gm. of precipitated antimony. Heat on a water-bath for twenty minutes while passing a slow stream of carbon dioxide through the flask. Boil briskly for two minutes, cool in an atmosphere of carbon dioxide and titrate at once with standard iodine solution.

The use of chloramine-T (p. 184) permits the reduction to be carried out with lead foil. The technique is the same as that for nickel, but the reduction must be allowed to proceed slowly for one and a half hours. When the solution is cold, an air-free solution of sodium hydroxide, with a little solid sodium carbonate, is added to it to reduce the concentration of free acid to about 3 per cent. and to maintain an atmosphere of carbon dioxide. After the addition of a crystal of potassium iodide and a few drops of starch solution, the tin is immediately titrated with a standard solution of chloramine-T.

#### Determination of Arsenic in its Compounds by means of Iodine

When iodine is added to a weakly-alkaline solution of arsenious oxide, the following reaction takes place:



This action is reversible; that is to say, under suitable conditions hydriodic acid will reduce arsenates. Therefore, in order to make the oxidation with iodine quantitative, the hydriodic acid must be removed as it is formed. A base such as sodium bicarbonate must be present. On the other hand, if the  $\text{P}_x$  of the

solution is too high, the iodine will be destroyed by the alkali with the production of hypiodides or iodates.

If pure arsenious oxide is available, a solution of iodine can be standardised by this method. This process only will be described, the determination of trivalent arsenic being merely its converse.

**Standard Solution of Arsenious Oxide.** The equivalent weight of arsenious oxide is 49.45. To make a litre of approximately decinormal solution, weigh out accurately about 4.945 gm. of the pure, resublimed oxide. Dissolve in a few millilitres of water containing some 4 gm. of sodium hydroxide. Dilute with water, add a drop of phenolphthalein, and titrate with dilute sulphuric acid until the indicator is just colourless. Transfer to a litre flask. Add 100 ml. of a saturated solution of sodium bicarbonate, and dilute to 1 litre. It is immaterial whether the iodine solution is run into the arsenite, or the arsenite into the iodine. Starch is used as indicator.

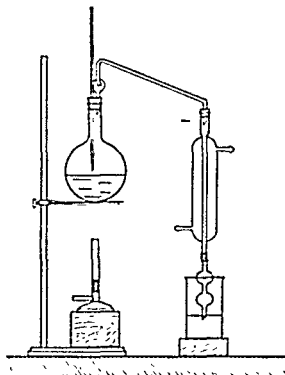


FIG. 82. DISTILLATION OF ARSENIC.

**Distillation of Arsenic.** If pentavalent arsenic is present, the method is more involved. The arsenic must be first reduced, and gaseous reducing agents, such as  $\text{SO}_2$ , cannot be used because it is difficult to remove the excess of reducing agent by distillation without some loss of the volatile  $\text{AsCl}_3$ . Probably the best method is to reduce the arsenic with  $\text{Cu}_2\text{Cl}_2$  in hydrochloric acid or with  $\text{FeSO}_4$ , and to distill over the  $\text{AsCl}_3$ .

An apparatus suitable for the distillation of small quantities of arsenic is shown in Fig. 82. The capacity of the distillation-flask should be at least 200 ml., and the thermometer bulb should be set about an inch above the surface of the liquid. The receiver should contain water in which to trap the arsenic chloride, and it must be cooled in a mixture of ice and water. All rubber stoppers and tubing must be free from sulphur. Precautions against "sucking back" must also be taken.

Place the liquid containing the arsenic in the flask, and add about 250 ml. of concentrated hydrochloric acid and 5 gm. of cuprous chloride. Distill until either about 150 ml. of liquid have been collected, or until the thermometer indicates a temperature of  $108^\circ \text{C}$ . It is always advisable to add a further 50 ml. of hydrochloric acid and a further 5 gm. of cuprous chloride, and to repeat the

distillation, collecting the second distillate in a fresh receiver. Meanwhile the arsenic in the first distillate may be titrated. The second distillation is essential if more than about 10 mgrm. of arsenic were present originally. Before titrating the distillate with iodine, add sodium hydroxide until it is just alkaline, then dilute hydrochloric acid until it is just acid, and then 20 ml. of a saturated solution of sodium bicarbonate.

When large quantities of arsenic are to be separated from other metals, the distillation must be conducted either in a stream of hydrochloric acid gas or in a mixture of that gas and sulphur dioxide. For details, consult specialised text-books (p. 518).

By distillation,  $\text{AsCl}_3$  (B.P.  $130^\circ \text{C.}$ ) can be separated from the less volatile  $\text{SbCl}_3$  (B.P.  $223^\circ \text{C.}$ ) and  $\text{SnCl}_4$  (B.P.  $620^\circ \text{C.}$ ), but not from  $\text{SnCl}_2$  (B.P.  $114^\circ \text{C.}$ ).

After the determination of the trivalent metal by iodine, it is often more convenient, in the absence of antimony and tin, to determine the total arsenic in a fresh sample either gravimetrically as  $\text{As}_2\text{S}_5$  after reduction by  $\text{SO}_2$  (p. 97), or as  $\text{Mg}_3\text{As}_2\text{O}_7$  after oxidation by  $\text{H}_2\text{O}_2$  (p. 79). A volumetric method for pentavalent arsenic is given on p. 258, and other methods for the trivalent element on pp. 181 and 182.

#### Determination of Antimony by Iodine

The determination of antimony by iodine is very similar to that of arsenic. The same limitations apply, but, in addition, antimony is usually insoluble in nearly neutral solutions. The presence of a tartrate is essential to prevent the precipitation of the metal.



For practice, weigh out accurately about 2 gm. of anhydrous tartar emetic,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ , dissolve in water, and dilute the solution to 250 ml. Transfer 50 ml. of this solution to a conical flask, and add an equal volume of a cold, saturated solution of  $\text{NaHCO}_3$  free from  $\text{Na}_2\text{CO}_3$ . Now pour in a few drops of starch solution, and add the iodine solution from a burette until a faint blue colour just appears. The blue colour will disappear when the liquid is stirred, and more iodine solution must be added until the faint blue tint persists.

In general, to a solution of the antimonious salt add tartaric acid in slight excess, and nearly neutralise with sodium hydroxide. Add the necessary volume of the saturated solution of sodium bicarbonate and carry out the above titration.

When *pentavalent antimony* is present, prepare a solution in very concentrated hydrochloric acid. Place this solution in a large flask and reduce the antimony by adding a few millilitres of a saturated solution of sodium sulphite from time to time. Boil vigorously to expel all sulphur dioxide, add a drop of phenolphthalein and run in potassium hydroxide solution until the red colour is produced. Add first a small excess of tartaric acid, then the sodium bicarbonate, and proceed as before.

#### Determination of Hydrogen Sulphide in Aqueous Solution by means of Standard Iodine Solution

When a sufficiently dilute solution of hydrogen sulphide is brought into contact with free iodine, the following reaction takes place:



Thus 253.8 gm. of iodine react with 34.08 gm. of  $\text{H}_2\text{S}$ .

If the solution, in which the  $\text{H}_2\text{S}$  is to be determined, contains more than 0.04 per cent. by weight of the gas, the change may not occur entirely according to the above equation. A solution of this concentration is 0.02 normal.

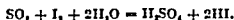
First dilute the hydrogen sulphide solution, if necessary, with recently prepared air-free water until it contains not more than 0.04 per cent. of the gas, and add rapidly a measured volume of the diluted solution to a known volume of a standard iodine solution, which must be in excess of the  $\text{H}_2\text{S}$ , and which must be feebly acidic. Then determine this excess with sodium thiosulphate, using starch as indicator. It is convenient to use 0.1 N. but not stronger standard solutions, although reliable results may be obtained if they are centinormal.

Although the  $\text{H}_2\text{S}$  solution can be titrated directly with iodine, the method recommended above is the better. A direct titration tends to give low results,

because of atmospheric oxidation, partial loss of  $\text{H}_2\text{S}$  by evaporation, and side-reactions.

#### Determination of Sulphur Dioxide, in Solution or in Combination, by Iodine and Thiosulphate

**Determination of Sulphurous Acid.** If a solution of sulphur dioxide gas is mixed with an excess of a standard iodine solution, the following reaction takes place :



It follows from the equation that 253.8 gm. of iodine correspond with 64.06 gm. of sulphur dioxide.

the iodine solution. If a considerable volume of the solution of sulphur dioxide is available, it may be stored as shown in Fig. 78, p. 135.

Ascertain by a preliminary trial in what proportions the solution of sulphur dioxide must be mixed with the iodine so as to leave the latter in very slight excess. Then introduce the required quantity of the standard iodine into a large flask and add water until the solution is very dilute. Acidify with a small quantity of dilute sulphuric or hydrochloric acid, and run in the sulphurous acid, slowly and with constant stirring. Titrate the small excess of iodine with sodium thiosulphate solution, using starch as indicator. Note that the  $\text{SO}_2$  solution must be added to the iodine solution; if iodine is added to the  $\text{SO}_2$ , reactions other than that expressed by the above equation take place.

**Determination of  $\text{SO}_2$  in Sulphite.** Weigh the finely-powdered, solid sulphite

such as calcium sulphite, is being analysed. Determine the excess of iodine by means of standard thiosulphate solution and starch. Repeat, using only a small excess of the decinormal iodine solution, and titrate this excess as before.

#### Determination of Formaldehyde by means of Standard Iodine and Sodium Thiosulphate Solutions

The solution, known commercially as "formalin," contains about 40 per cent. of formaldehyde. Formaldehyde may be determined by oxidising it to formic acid by means of iodine in alkaline solution.



It will be seen that each molecule of free iodine corresponds with one molecule of formaldehyde. Note that the oxidation will not take place in acid solution.

For the determination, dilute 5 ml. of the formalin to 200 ml. Introduce 10 ml. of this approximately 1 per cent. solution of formaldehyde into a conical flask and add 100 ml. of decinormal iodine solution. At once add sodium hydroxide solution, drop by drop, until the colour of the liquid becomes bright yellow. A common error is to add here an insufficient quantity of the sodium hydroxide. Allow the reaction to proceed for at least ten minutes, acidify with dilute hydrochloric acid, and titrate the liberated iodine with decinormal sodium thiosulphate solution. Each millilitre of decinormal iodine solution, which has been used to oxidise the formaldehyde, corresponds with 0.0015 gm. of that compound.

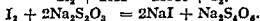
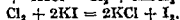
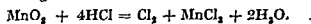
#### USE OF STANDARD SODIUM THIOSULPHATE SOLUTION WITH POTASSIUM IODIDE

Many oxidising agents have the power of liberating an equivalent quantity of iodine from a solution of potassium iodide. Thus free chlorine reacts with potassium iodide solution in the following manner :

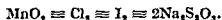


As the iodine can easily be determined with standard sodium thiosulphate, the reaction is frequently adapted for use in volumetric analysis. As an example, the standardisation of a solution of sodium thiosulphate against the iodine liberated from an excess of potassium iodide by a known weight of potassium iodate or of potassium permanganate, in the presence of acid, has already been described (pp. 129 and 140).

Certain oxidising agents will not react quantitatively with potassium iodide, but they will attack hydrochloric acid with the liberation of an equivalent quantity of chlorine. This, in turn, may be made to react with a solution of potassium iodide, and the liberated iodine may be titrated. By means such as this, the applications of the method can be greatly extended. As an example, consider the determination of manganese dioxide by the following chain of reactions :



Whence



### Determination of Chlorine in Aqueous Solution

Mix a measured quantity of a dilute solution of chlorine with a solution of potassium iodide in excess (*Note*). Then determine the amount of iodine liberated, by titration with standard sodium thiosulphate solution ; 35.46 grm. of chlorine liberate 126.9 grm. of iodine.

*Note.* The most satisfactory method in excess is to mix the chlorine with the standard thiosulphate solution, after the addition of potassium iodide. If the two titrations yield identical results, the potassium iodide solution was originally present in excess.

### Evaluation of Bleaching-powder by means of KI and Thiosulphate

Prepare the suspension of bleaching-powder as described on p. 153. After this liquid has been mixed by shaking, transfer 25 ml. of it to a 250-ml. flask, add an excess of potassium iodide solution, and acidify the liquid with dilute acetic acid. Then determine the amount of iodine which has been liberated, by means of sodium thiosulphate solution, using starch as indicator.

The amount of "available chlorine" present in the bleaching-powder is chemically equivalent to the iodine liberated.

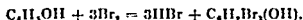
of the  
is not

Other Methods for "available chlorine" in bleaching-powder are described on pp. 152 and 184.

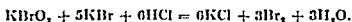
### Determination of Bromine and Phenol in Aqueous Solution

The bromine solution is diluted, if necessary, and is added to an excess of potassium iodide solution. The iodine, which is liberated by the bromine, is then titrated by standard thiosulphate solution.

A method for determining phenol is based on this reaction. Phenol reacts with bromine as follows :



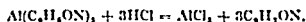
The phenol is treated with an excess of a solution of bromine, or, better, with an excess of a solution of potassium bromate and potassium bromide, which should contain at least 3.6 times as much potassium bromide as potassium bromate. The excess of bromide plays no part in the reaction and does not interfere. On treating this mixture with concentrated hydrochloric acid, the bromate is quantitatively destroyed, with liberation of bromine :



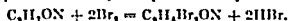
The bromine is allowed to react with the phenol for at least half an hour. The flask should be shaken occasionally. Then an excess of potassium iodide is added and the liberated iodine is titrated with standard sodium thiosulphate.

### Determination of Aluminium and Magnesium indirectly with 8-Hydroxyquinoline (Oxine)

The complex compounds of aluminium or magnesium with 8-hydroxyquinoline are easily decomposed by hydrochloric acid, which liberates the latter :



The hydroxyquinoline is easily and quantitatively brominated :



If an excess of bromine is used, this excess may be determined by titration with sodium thiosulphate, after the addition of potassium iodide, and using starch as indicator. These reactions are made the basis of a method for the determination of aluminium and magnesium. The equations show that twelve atoms of bromine are equivalent to one atom of aluminium. In a similar way it may be shown that eight atoms of bromine are equivalent to one atom of magnesium.

Precipitate the aluminium or the magnesium by the methods described on pp. 65 and 77, respectively. Collect the precipitate, preferably in a coarse-grade, sintered-glass crucible, and wash it thoroughly with hot ammoniacal water to get rid of all traces of uncombined oxine. Dissolve the aluminium precipitate in warm, concentrated hydrochloric acid; the magnesium in concentrated acid, diluted with four times its own volume of water. From this point, the procedure is the same for both metals.

Titrate the solution slowly with standard bromate-bromide mixture of approximately decinormal concentration with respect to the bromate, making certain that the weight of potassium bromide present in this mixture is at least four times that of the bromate. A decinormal solution of potassium bromate contains 2.763 gm. of the salt per litre (see equation under determination of phenol, above). Add the bromate in slight excess.



As the colour of the bromine is difficult to detect, it is best to take out a drop of the solution from time to time and to see whether this drop will set iodine free on filter-paper which has been damped with a mixture of potassium iodide and starch solution. When free bromine is present, dilute with 20 per cent. hydrochloric acid, add a few millilitres of 10 per cent. potassium iodide solution and titrate the liberated iodine with a standard, approximately decinormal sodium thiosulphate solution, using starch as indicator.

*Note.* Methyl orange has been used as an indicator for this titration since it is rapidly decolorised by the slightest excess of bromine. Since, however, decolorisation may in certain cases occur before the equivalence point is reached, 2 to 3 drops of a 0.1 per cent. solution of fluorescein in very dilute NaOH solution are preferable. The colour turns from greenish-yellow to reddish-brown at the end-point by reason of the formation of eosin by the action of the bromine on the fluorescein, which incidentally, also behaves as a fluorescent indicator (p. 253) in this reaction.

The use of bromate solutions containing up to 10 grm. of potassium bromate per litre is reasonable, but in no case should more than 20 mg. of aluminium or magnesium be precipitated.

The Method of Calculation is illustrated by the following example :

In a determination of the percentage of aluminium in a sample of potash alum, the aluminium in 0.0704 grm. of the alum was precipitated with "oxine." The compound was isolated, dissolved in hydrochloric acid, and 23.0 ml. (excess) of bromate-bromide mixture containing 2.730 grm. of potassium bromate per litre were added to the solution. A volume of 3.7 ml. of a sodium thiosulphate solution was found to be equivalent to the excess of bromine, and 26.7 ml. of the thiosulphate were required to titrate the iodine set free from potassium iodide by 25 ml. of the bromate mixture.

<i>Oxidising Agents.</i>	<i>Reducing Agents.</i>
25 ml. of bromate $\equiv$ 26.7 ml. of $\text{Na}_2\text{S}_2\text{O}_3$ .	
23.0 ml. of bromate $\equiv$ 3.7 ml. of $\text{Na}_2\text{S}_2\text{O}_3$	+ aluminium-"oxine."

Whence

$$3.7 \text{ ml. of } \text{Na}_2\text{S}_2\text{O}_3 \equiv \frac{25.0 \times 3.7}{26.7} \\ = 3.46 \text{ ml. of bromate.}$$

Therefore the aluminium is equivalent to the bromate in  
(23.0 - 3.46) = 19.54 ml. of bromate,

or to  $\frac{19.54 \times 2.730}{1000}$  grm. of bromate.

But  $\frac{2\text{KBrO}_3}{2 \times 167.0} \equiv \frac{12\text{Br}}{26.97} \equiv \text{Al.}$

Therefore

$$\frac{19.54 \times 2.730}{1000} \text{ grm. of KBrO}_3 \text{ is equivalent to } \frac{26.97 \times 19.54 \times 2.730}{1000 \times 2 \times 167.0} \\ = 0.00431 \text{ grm. of aluminium.}$$

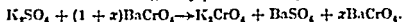
The percentage of aluminium is  $\frac{0.00431 \times 100}{0.0704} = 5.43$ .

### Determination of Barium, Lead and Sulphate by KI and Thiosulphate

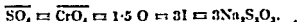
The metals are precipitated as chromates, which are dissolved in a suitable solvent. The chromic acid produced is allowed to react with

an excess of potassium iodide, and the free iodine is titrated with standard sodium thiosulphate solution.

A sulphate is determined by adding an excess of a solution of barium chromate in hydrochloric acid. Barium sulphate is precipitated, and the solution will contain the excess of barium chromate together with the chromate of the metal originally present as sulphate :



The barium chromate is precipitated by the addition of ammonia, and the chromate left in solution will be equivalent to the sulphate originally present. The precipitate is removed and the filtrate, after acidification, is treated with an excess of potassium iodide, and the free iodine is determined.



**Barium.** The solution for analysis should contain about 0.1 grm. of the metal and should have a volume of about 50 ml. Add to it 10 ml. of a 20 per cent. solution of ammonium acetate in a 500-ml. beaker. Precipitate the barium by adding 15 ml. of a concentrated solution of potassium dichromate (100 grm. per litre) to the boiling liquid. Continue to boil for at least a minute after the addition of the precipitant. Filter through a Gooch crucible, and wash the precipitate and the beaker with hot water. Loosen the precipitate in the crucible and transfer precipitate, asbestos and crucible, to the original beaker. Digest in the cold with 100 ml. of 25 per cent. hydrochloric acid. Dilute to 200 ml. Add 6 grm. of KI, and titrate, after ten minutes, with thiosulphate. When near the end-point, add starch and continue to run in the thiosulphate until the blue colour is faint. Then add 10 ml. of concentrated hydrochloric acid, heat to 40° C., and finish the titration.

**Lead.** The lead chromate is precipitated either as directed on p. 74 or as in Method I., p. 154. Collect and wash on filter-paper. Dissolve the precipitate in a solution made by adding 30 ml. of 50 per cent. hydrochloric acid to 100 ml. of a saturated solution of sodium chloride. Wash the paper first with at least 50 ml. of this solution, then with cold water. Add 2 grm. of potassium iodide, and titrate at once with sodium thiosulphate, adding starch when near the end-point.

This method is unreliable unless the sodium thiosulphate has been standardised against a known weight of lead by the same procedure.

**Sulphate.** First prepare a solution of barium chromate as follows: Weigh out accurately equivalent quantities of pure barium chloride and pure potassium chromate (say, 1.22 grm. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and 0.97 grm. of  $\text{K}_2\text{CrO}_4$ ), and dissolve them separately in hot water. Mix the two solutions. Wash the resulting precipitate repeatedly with hot water by decantation. Add about 1 litre of water and 50 ml. of concentrated hydrochloric acid, in that order, and shake until the precipitate has dissolved. The whole of this solution will then be equivalent to about 0.5 grm. of sulphuric acid. The solution deteriorates on keeping.

The solution for analysis should not contain more than 20 milligrammes of the  $\text{SO}_4$  radical. Neutralise it, if necessary, heat it to boiling, and add

the barium chromate solution in slight excess. After boiling for at least five minutes longer, precipitate the excess of barium chromate by the careful addition of ammonia in slight excess, until a pale yellow colour just appears in the liquid. Cool, and make up to 500 ml. Filter through a dry paper into a measuring-cylinder. Collect 250 ml., transfer the liquid to a conical flask, and add 2 gm. of KI and 5 ml. of concentrated hydrochloric acid. Close the neck of the flask with a cork. After fifteen minutes, titrate with standard and approximately 0.05 N. sodium thiosulphate solution.

This method is more rapid than the gravimetric determination of sulphate as barium sulphate, but the results are not nearly so reliable.

**Benzidine Method.** The reaction of the soluble benzidine hydrochloride with a soluble sulphate to form the insoluble benzidine sulphate provides a more accurate though somewhat less rapid volumetric method.

The reagent is prepared by grinding 6.7 gm. of benzidine with 20 ml. of water and it  
fro  
sin  
we

phate to benzidine and sulphuric  
ii, with phenolphthalein as indicator,  
Then 1 ml. of 0.1 N. NaOH =

inone both produce a red-brown colour with a barium salt, and they may therefore, be used to indicate the end-point of the titration of a sulphate with such a reagent. However, for reasons indicated on p. 66 the reaction is not really suitable for a direct titration, and  
Cl<sub>2</sub> solution  
confined to  
where the

### Determination of Manganese Dioxide by means of KI and Thiosulphate

The manganese dioxide is heated with an excess of concentrated hydrochloric acid, and chlorine equivalent to the "available" oxygen in the dioxide is evolved. This gas is passed into an excess of potassium iodide solution, and the iodine which is set free is determined by means of standard sodium thiosulphate. The equation on p. 170 shows that 86.9 gm. of MnO<sub>2</sub> will liberate 70.91 gm. of chlorine, which are equivalent to 253.8 gm. of iodine.

The Apparatus shown in Fig. 83, will be found useful for carrying out this determination. It is prepared as follows:

A small flask or bulb-tube (a), of about 60 ml. capacity, is connected with a tube (b) by means of a rubber joint, inside which the ends of the glass tubes are in contact.

To the end of (b) is fused a narrow tube (c), which is bent as is shown in the figure, and is fitted to the bulbed U-tube (d) by means of a rubber bung. This apparatus will be found sufficient for ordinary purposes, but in the figure an additional plain U-tube (e) is shown, which may be used as a guard-tube to prevent the escape of any chlorine or iodine. These U-tubes are kept cool by immersing them in cold water contained in a beaker.

A plain, bent, glass tube, of the same diameter throughout as the neck of the flask, may replace the tubes (b) and (c). The rubber bungs and connections which are used in fitting up this apparatus should have previously been freed from sulphur by boiling them in a solution of sodium hydroxide for a short time. For accurate determinations it is better to use an apparatus fitted throughout with ground-glass connections.

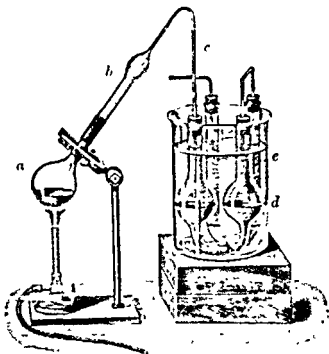


FIG. 83. ABSORPTION OF CHLORINE IN KI SOLUTION.

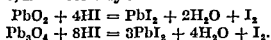
**Procedure:** Weigh out accurately about 0.5 gm. of finely-powdered manganese dioxide into the flask (a). Half fill the bulbs of the U-tube (d) with a solution containing about 3 gm. of potassium iodide. If the second U-tube (e) is also used, pour into it sufficient of a more dilute potassium iodide solution to fill the bend. Ascertain that the apparatus is air-tight, and then add about 20 ml. of concentrated hydrochloric acid to the dioxide in the flask.

It will be found convenient to introduce a small piece of magnesite with the manganese oxide. On the addition of the acid, a regular stream of carbon dioxide will then flow through the U-tubes with the chlorine, and this will dilute the chlorine and allow the absorption to proceed more smoothly. Heat the flask gently over a small flame, and, as soon as the manganese dioxide has completely dissolved, boil the acid until all the chlorine has been expelled.

As soon as all the chlorine has passed into the absorption tubes, pour out the contents of the U-tubes through a funnel into a 250-ml. measuring-flask. Rinse out the tubes, using a solution of potassium iodide if solid iodine has been deposited in them, and add these rinsings to the contents of the flask. Make up the liquid to the mark, mix it well, and titrate 20 ml. of it with standard sodium thiosulphate solution in the presence of starch. The weight of iodine thus found is a measure of the chlorine which has been liberated by the manganese dioxide.

### Determination of Lead Dioxide and Red Lead by means of KI and Thiosulphate

These substances react directly with hydrochloric acid under suitable conditions and therefore distillation with hydrochloric acid, as in the case of manganese dioxide, is unnecessary :



Before titrating the iodine with thiosulphate, a clear solution must be obtained. This is accomplished by the addition of a sufficient quantity of sodium acetate and by the use of a comparatively small quantity of potassium iodide. The precipitation of lead iodide is thus prevented.

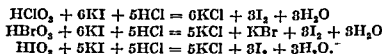
**Lead Dioxide.** Add about 10 grm. of sodium acetate and 0.3 to 0.5 grm. of the sample of lead dioxide (which must be accurately weighed) to 5 ml. of 5 per cent. acetic acid. Add also 1.2 grm. ( $\pm 10$  per cent.) of potassium iodide, and dilute to 25 ml. with water. Shake occasionally until solution is complete. If there is a persistent precipitate of lead iodide, add an additional 3 to 5 grm. of sodium acetate, together with a few millilitres of water. Without further dilution, titrate with standard sodium thiosulphate solution, using starch as indicator.

Sometimes the sample of lead dioxide is granular and will not react completely with hydriodic acid, even when it is finely ground and after being allowed to stand in contact with the reagents for a long time. In this case, use the method described on p. 159.

**Red Lead.** The general method is the same as for lead dioxide (see above). Take about 1 grm. of the sample, but double quantities of sodium acetate and potassium iodide, in 20 ml. of 25 per cent. acetic acid. When solution is complete, dilute to 50 ml. with water, adding a further 5 grm. of sodium acetate, or sufficient additional sodium acetate to keep the lead iodide in solution. Titrate as before.

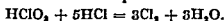
### Determination of Chlorates, Bromates and Iodates with KI and Thiosulphate

These radicals react with potassium iodide in the presence of dilute hydrochloric acid as follows :



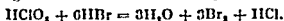
The first reaction is very slow, the second is sluggish and the third is extremely fast. The third reaction has already been discussed (p. 163), and will not be described further here.

**Chlorates.** Because of the slowness of the reaction given above, it is perhaps best to distil the chlorate with concentrated hydrochloric acid, using the apparatus shown in Fig. 83, p. 175, and to collect the liberated chlorine in a concentrated solution of potassium iodide.



Take 0.5 grm. of potassium chlorate, and distil it with concentrated hydrochloric acid. Make up the solution of iodine to 250 ml. and titrate 25 ml. with standard, approximately decinormal sodium thiosulphate solution.

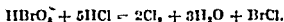
*Alternatively, digest the chlorate with cold hydrobromic acid.*



The bromine is then allowed to react with potassium iodide. These reactions are completed in a reasonably short time.

Dissolve an accurately weighed quantity of about 1 grm. of potassium chlorate in water, and make up to 500 ml. to give an approximately decinormal solution. Take 25 ml. of this solution in a large stoppered bottle, and add 1 grm. of solid potassium bromide and 50 ml. of concentrated hydrochloric acid. After five minutes, add 1 grm. of potassium iodide, dilute considerably, and titrate with standard sodium thiosulphate, using starch as indicator.

**Bromates.** In this case, a distillation with hydrochloric acid is unnecessary. If it is carried out, note that one molecule of bromate produces only four atoms of chlorine.

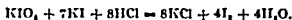


The bromine monochloride is not volatile and remains in the flask.

Bromates in solution are easily determined by adding a considerable excess of solid potassium iodide and a large volume of concentrated hydrochloric acid. After a few minutes and suitable dilution the iodine may be titrated with sodium thiosulphate in the presence of starch. However, the reaction between bromic acid and hydriodic acid is catalysed by ammonium molybdate, and the presence of 2 or 3 drops of a solution of this reagent enables the iodine to be produced almost instantaneously, even when the concentration of hydrochloric acid is so low as 20 grm. per litre.

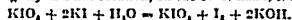
#### Determination of a Mixture of Iodate and Periodate

Periodates, in the presence of hydrochloric acid, react with potassium iodide as follows:



Periodates can therefore be determined by the method described for the determination of iodates (p. 163).

In neutral or slightly alkaline solution, on the other hand, the reaction is:



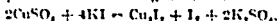
This iodine must be titrated with a standard solution of sodium arsenite (pp. 166 and 184).

If iodates and periodates are present together, add to a portion of the solution an excess of potassium iodide and dilute hydrochloric acid. Titrate the liberated iodine with sodium thiosulphate solution, using starch. This volume gives a measure of the total oxidising power of the solution.

Add 1 drop of phenolphthalein to a second portion of the solution and then carefully add hydrochloric acid or sodium hydroxide as required until the red colour of the phenolphthalein is just apparent. After the addition of 10 ml. of a cold, saturated solution of sodium bicarbonate, add potassium iodide, and titrate the liberated iodine with standard sodium arsenite, with starch as indicator. The result is a measure of the quantity of periodate present.

#### Indirect Determination of Copper in Solution by means of KI and Thiosulphate

The method depends on the following reaction:



The potassium iodide is added in excess to the weakly-acidified copper solution, the liquids are thoroughly mixed, and the iodine liberated is

titrated with standard sodium thiosulphate solution. The amount of iodine so found is proportional to the amount of copper which was originally present in solution. As a stoichiometric proportion of iodine may not be liberated, it is best to standardise the solution of sodium thiosulphate against pure copper by the method given below. Then as an exercise determine, under exactly the same conditions, the percentage of copper in a salt such as copper ammonium sulphate, or in a brass. In the latter case, take portions of about 0.25 grm. of the alloy, which should contain not more than traces of iron.

**Standardisation of the Sodium Thiosulphate Solution.** Weigh out accurately three or four portions, each of about 0.15 grm., of pure copper foil. Place each separately in a conical flask and add a *small quantity* (2 or 3 ml.) of nitric acid diluted with its own volume of water. Warm gently until all the copper has gone into solution, and then more strongly to get rid of all traces of oxides of nitrogen. As nitrous acid will react with potassium iodide, the complete removal of all oxides of nitrogen is most important. Cool. Cautiously add sodium carbonate solution until there is a permanent precipitate of copper carbonate. Just re-dissolve by adding dilute acetic acid in very slight excess. It is important at this stage that the solution be concentrated. It may be more convenient to dissolve the copper carbonate in concentrated acetic acid, to re-precipitate it with a very dilute solution of sodium carbonate and to re-dissolve this precipitate in the dilute acetic acid.

The solution is now ready for the addition of potassium iodide. Add the solid crystals in considerable excess. A weight of 3 grm. should be sufficient. Allow the flask to stand for at least five minutes, shaking it occasionally. Dilute to 150 to 200 ml., and titrate with sodium thiosulphate of approximately decinormal concentration until the colour of the iodine has almost disappeared. Add starch as indicator and complete the titration. Note that the cuprous iodide is not pure white in colour, but has a purplish tinge. In spite of this, the end-point is usually obvious, but if there is difficulty in recognising it when all the iodine has been reduced, add 1 drop of decinormal silver nitrate towards the end of the titration. Silver iodide will be precipitated, and to some extent its yellow colour will counteract the purple colour of the cuprous iodide. If the solid cuprous iodide still interferes, it can be dissolved as a complex salt by the addition of a large excess of potassium iodide.

The return of the starch-iodide colour after an apparent excess of sodium thiosulphate has been added will probably be due to one of three causes :

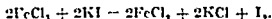
- (i.) The use of an insufficient quantity of potassium iodide, or the failure to allow enough time for the cupric ion to react with the iodide.
- (ii.) The incomplete removal of all nitrous acid.
- (iii.) The presence of a weak oxidising agent, such as a ferric salt. In this case the solution will also probably be too acidic.

Test for bromine with damped, starch-iodide paper. Cool. Transfer to a 250-ml. flask and make up to the mark. Take 25 ml. of this solution and adjust the acidity as described above.

For less accurate work, it will be sufficient to standardise the sodium thiosulphate against a standard solution of copper sulphate made up by weighing. A decinormal solution of this salt contains 24.97 grm. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre.

### Determination of Ferric Salts by KI and Thiosulphate

The method is based on the following reaction :



The reaction is somewhat slow and it is also reversible, ferrous chloride being oxidised by iodine in the presence of a large quantity of concentrated hydrochloric acid. Time must be allowed for the reaction to take place, a considerable excess of potassium iodide must be used, and the concentration of hydrochloric acid must be less than normal. Also, as hydriodic acid is most easily oxidised by atmospheric oxygen in the presence of ferrous iron, the vessel in which the reaction is taking place must be kept closed.

To 25 ml. of the approximately decinormal solution of ferric iron for analysis, in a bottle or conical flask, add sodium hydroxide until the solution is nearly neutral, as shown by the failure of the alkali to precipitate more ferric hydroxide. Add hydrochloric acid, taking care to keep the total concentration of this acid in the solution below normal, and 3 grm. of potassium iodide. Close the vessel and allow it to stand for five minutes. Titrate with standard sodium thiosulphate in the presence of starch as indicator.

*Note 1.* It is obvious that other compounds which react with hydriodic acid must be absent. Among these must be counted nitric acid (and nitrates) which will liberate iodine in the presence of iron.

*Note 2.* The method described above is satisfactory and not unduly slow. The time can be shortened, however, by the addition of a small quantity of pure cuprous iodide suspended in water; this acts as a catalyst.

### Determination of Hydrogen Peroxide by means of KI and Thiosulphate

Hydrogen peroxide, in very dilute solution, reacts with hydriodic acid as follows :—



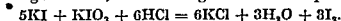
Take a suitable quantity of the solution of hydrogen peroxide in a measuring-flask and dilute it to standard volume (see p. 159). This solution should contain not more than 5 grm. of the peroxide per litre. Put 100 ml. of dilute (10 per cent.) sulphuric acid, 100 ml. of water and about 2 grm. of potassium iodide into a stoppered bottle. Add 10 or 20 ml. of the peroxide solution, slowly and with constant movement of the liquid. Stopper the bottle to prevent oxidation of the hydriodic acid by atmospheric oxygen, and put it aside for five minutes to allow the reaction to reach completion. Titrate the free iodine with standard sodium thiosulphate, using starch as indicator.

*Note.* This method is preferable to the permanganate method (p. 160) in that it is not affected by reducing agents such as glycerol.



## USE OF STANDARD POTASSIUM IODATE SOLUTION

When a solution of potassium iodate is allowed to run into a solution of potassium iodide acidified with hydrochloric acid, the iodide at first necessarily being in excess, the following reaction takes place :



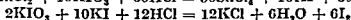
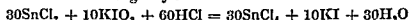
When the concentration of hydrochloric is low, this reaction proceeds until all the iodide is destroyed, the excess of iodate remaining unchanged ; but in the presence of much hydrochloric acid, the excess of iodate reacts with the iodine to form iodine monochloride as follows :



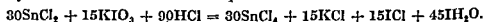
If, then, a solution of potassium iodate is run into a solution of potassium iodide in the presence of a high concentration of hydrochloric acid, at first the iodide is oxidised to iodine with the production of the well-known brown colour. Later this colour diminishes, and at the end-point the solution is coloured only a pale yellow by the iodine monochloride. The complete equation for the reaction, the sum of the two equations already set out, is :



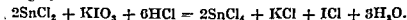
It will be obvious that free iodine and iodides can be determined by this method. Further, any reducing agent which reacts with potassium iodate in an acidified solution will produce hydriodic acid, and this, in turn, will react with more iodate to produce iodine, which will react with still more iodate to produce iodine monochloride. A reducing agent can therefore be determined by these successive reactions. As an example, consider the reactions between stannous chloride and potassium iodate. The successive reactions which occur are best described by writing the equations in the following way :



By the addition of these three equations :



Or, dividing by 15 :



Hence, provided a large quantity of hydrochloric acid is present, two molecules of stannous chloride are oxidised to stannic chloride by one molecule of potassium iodide. Under these conditions, therefore, a normal solution of potassium iodate contains one-quarter of the gramme-molecular weight of the salt per litre.

*Note.* This method can also be used to determine the amount of acid and it then reacts with iodate to form iodine monochloride as described on p. 163.

## Determination of Iodides or Iodine by Potassium Iodate

Place a suitable quantity of the substance for analysis (about 0.2 gm. of KI) in a well-stoppered bottle of about 250 ml. capacity, together with

about 50 ml. of water and an equal volume of concentrated hydrochloric acid. Add about 5 ml. of carbon tetrachloride or chloroform. Run in decinormal potassium iodate solution (5.35 gm. of  $\text{KIO}_3$  per litre) until the pale brown colour of the aqueous layer shows that nearly all the iodine has been converted to monochloride. Stopper the bottle and shake it vigorously. Continue to add small volumes of the iodate solution, shaking vigorously for each addition, until the violet colour of the carbon tetrachloride layer has disappeared.

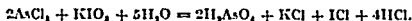
If the concentration of hydrochloric acid has been reduced below 33 per cent. by volume by the addition of the aqueous solution of potassium iodate, sufficient acid to raise the content to 33-50 per cent. by volume must be added to prevent the hydrolysis of the iodine monochloride.

A mixture of Iodine and Iodide can be analysed, by first titrating the iodine with sodium thiosulphate, and then by determining the iodine plus iodide in a fresh sample with potassium iodate.

### Determination of Arsenic or Antimony by Potassium Iodate

The solution should contain about 3-7 gm. of trivalent arsenic or antimony per litre. For practice, weigh out accurately about 1.2 gm. of arsenious oxide. Dissolve this in a small quantity of a hot solution of sodium hydroxide, cool, and make up to 250 ml. Take 25 ml. of this solution in a glass bottle provided with a tightly-fitting glass stopper. Add some 5 ml. of chloroform, and enough water and hydrochloric acid to bring the volume of the aqueous solution to about 50 ml. and the concentration of the hydrochloric acid to about 50 per cent. by volume.

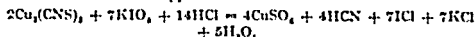
Run in the iodate from a burette. Iodine will be liberated at first. This will colour the chloroform and, to some extent, the solution. When all the arsenic has been oxidised, the iodate reacts with the iodine to give the monochloride and the colour gradually disappears. Near the end-point, add the iodate slowly, and shake the bottle vigorously. The end-point is reached when the chloroform is colourless and has remained colourless for five minutes.



### Determination of Copper by Potassium Iodate

Thiocyanic acid, in the presence of concentrated hydrochloric acid, is oxidised by potassium iodate to a mixture of hydrocyanic and sulphuric acids. This reaction is used for the determination of metals which can be precipitated as thiocyanates from solution (p. 61): e.g., copper, as  $\text{Cu}(\text{CNS})_2$ , and zinc, as  $\text{ZnHg}(\text{CNS})_2$ .

The determination of copper is described below.



About 0.02 gm. of copper is a weight suitable for titration with potassium iodate solution containing 5 gm. of the salt per litre.

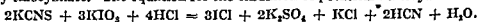
Prepare a suitable solution of copper or copper sulphate, making sure that no oxidising agent is present. Precipitate the copper in an aliquot portion of this solution as thiocyanate, following the instructions given on p. 61. Filter the precipitate after ten minutes through ordinary filter-

paper, and wash the precipitate free of all excess of the thiocyanate reagent.

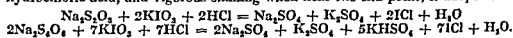
Transfer the filter-paper with the precipitate to a bottle fitted with a glass stopper. Remove any traces of precipitate left in the vessel used for the precipitation by wiping it round with a small piece of dry filter-paper, which is also put into the bottle. Add about 5 ml. of chloroform, and enough water and hydrochloric acid to make the volume about 50 ml. and the acid content about 50 per cent. by volume (p.181). Titrate with standard potassium iodate as described on p. 180. If more convenient, two or three times as much copper may be taken, in which case, titrate with a more concentrated solution of potassium iodate.

#### Determination of Thiocyanates, Sulphates, Thiosulphates and Tetrathionates by Potassium Iodate

The iodine monochloride method for cuprous thiocyanate may be adapted to any thiocyanate. The equation for the oxidation of potassium thiocyanate is :



Thiosulphates and tetrathionates also react quantitatively with potassium iodate, provided that the standard procedure, namely, addition of 5 ml. of chloroform as indicator, presence of 33 to 50 per cent. by volume of concentrated hydrochloric acid, and vigorous shaking when near the end-point, is adopted.



*Note.* Considerations of space prevent other examples of this excellent method from being given. The method of certain oxidising agents, notably to react with potassium iodide iodate. For details and for the (Lang's method) consult *Sutton's*

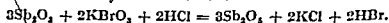
#### USE OF POTASSIUM BROMATE SOLUTION

##### Determination of Arsenic, Antimony and Tin

When an acidified solution containing trivalent arsenic or antimony, or divalent tin, is treated with a solution of potassium bromate, the bromate is partially reduced to bromide, the bromic and hydrobromic acids react to produce bromine, and this bromine at first oxidises the metal. When all the metal has been oxidised, free bromine appears. This marks the end-point, but, as the colour of the bromine is not intense, the end-point is difficult to see. This is overcome by adding an organic dyestuff (*e.g.*, methyl orange or methyl red). This dyestuff is oxidised and its intense colour is destroyed by the bromine, but only after the metal has been completely oxidised.

This method, details of which are given below, is highly recommended for arsenic, antimony and tin in ores and alloys.

**Arsenic or Antimony.** Prepare a decinormal solution of potassium bromate by dissolving 2.783 grm. of the salt (which should have been dried at 110° C.) in water and diluting to 1 litre. This solution should be standardised against a known weight of the metal to be determined. Thus, trivalent antimony is oxidised as follows :

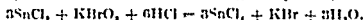


Dissolve an accurately-weighed quantity of about 0.2 gm. of finely-powdered antimony in 20 ml. of concentrated hydrochloric acid to which a few drops of bromine have been added. Use a covered beaker and warm the liquid, shaking it occasionally. When the metal has dissolved, remove the excess of bromine by evaporation, cool, and add cautiously about 1 gm. of sodium sulphite to reduce the antimony. Remove the excess of  $\text{SO}_2$  by evaporation. To do this, the volume of the liquid must be reduced by about one-half, and if any arsenic happens to be present it will necessarily be lost by volatilisation as chloride. Wash down the cover and the sides of the beaker with hot water. Add that volume of concentrated hydrochloric acid which is equal to one-quarter of the volume of the liquid already present, heat to  $80^\circ \text{C}$ ., and run in slightly less than the calculated quantity of bromate. Add 3 drops of methyl orange and continue to run in the bromate, slowly, with continual shaking, until the colour of the dye disappears. Wait one minute, and then add another drop of indicator to make quite sure that the end-point has been reached.

The percentage of antimony in an alloy, after the removal of interfering elements, can be determined by exactly the same process; so also can the quantity of antimony in a solution. In the latter case, reduction with  $\text{SO}_2$  may not be necessary.

The titration of trivalent arsenic follows the same lines as the antimony titration, although, for arsenic, the concentration of hydrochloric acid need not be so high.

**Tin.** *Method 1.* Place the solution, which should contain 0.15 to 0.2 gm. of tin and should be faintly acid with hydrochloric acid, in a 200-ml. conical flask. This flask should be fitted with a Bunsen valve (p. 142). To the cold solution add about 0.15 gm. of aluminium wire, which should have been cut into short lengths. When all the tin has been precipitated, add 50 ml. of 50 per cent. hydrochloric acid and heat gently until all the tin has dissolved. Slip off the rubber cap of the Bunsen valve and connect the glass tube at once to a Kipp apparatus which is producing  $\text{CO}_2$ . Cool in an atmosphere of carbon dioxide. Titrate with decinormal potassium bromate solution, using methyl orange as indicator.



*Method 2.* As in the first method, precipitate the tin with aluminium wire and then dissolve it in hydrochloric acid. A 500-ml. flask with a round bottom should be used for these operations. The flask should be tightly stoppered with a rubber bung, through which pass the stem of a separating-funnel and a second tube fitted with a stop-cock and with a Bunsen valve. Before dissolving the precipitated tin in hydrochloric acid, it is well to add a piece of magnesite to ensure that all air will be removed from the flask. When the tin and magnesite have dissolved and it is judged safe to do so, close the stop-cock of the second tube and cool the flask. A partial vacuum should be produced.

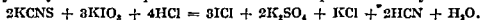
Place in the separating-funnel a solution containing a known volume of decinormal potassium bromate, in quantity more than sufficient to oxidise the tin; and potassium bromide in considerable excess over the residual bromate (0.5 to 1 gm. of  $\text{KBr}$ ). This solution should not contain

paper, and wash the precipitate free of all excess of the thiocyanate reagent.

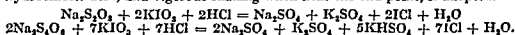
Transfer the filter-paper with the precipitate to a bottle fitted with a glass stopper. Remove any traces of precipitate left in the vessel used for the precipitation by wiping it round with a small piece of dry filter-paper, which is also put into the bottle. Add about 5 ml. of chloroform, and enough water and hydrochloric acid to make the volume about 50 ml. and the acid content about 50 per cent. by volume (p.181). Titrate with standard potassium iodate as described on p. 180. If more convenient, two or three times as much copper may be taken, in which case, titrate with a more concentrated solution of potassium iodate.

#### Determination of Thiocyanates, Sulphates, Thiosulphates and Tetrathionates by Potassium Iodate

The iodine monochloride method for cuprous thiocyanate may be adapted to any thiocyanate. The equation for the oxidation of potassium thiocyanate is :



Thiosulphates and tetrathionates also react quantitatively with potassium iodate, provided that the standard procedure, namely, addition of 5 ml. of chloroform as indicator, presence of 33 to 50 per cent. by volume of concentrated hydrochloric acid, and vigorous shaking when near the end-point, is adopted.



Note. Consideration of these and other examples of this excellent method . . . . . iodate. For details and for the use of the analogous iodine cyanide method (Lang's method) consult *Sutton's Volumetric Analysis* (12th Edition).

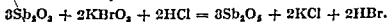
#### USE OF POTASSIUM BROMATE SOLUTION

##### Determination of Arsenic, Antimony and Tin

When an acidified solution containing trivalent arsenic or antimony, or divalent tin, is treated with a solution of potassium bromate, the bromate is partially reduced to bromide, the bromic and hydrobromic acids react to produce bromine, and this bromine at first oxidises the metal. When all the metal has been oxidised, free bromine appears. This marks the end-point, but, as the colour of the bromine is not intense, the end-point is difficult to see. This is overcome by adding an organic dyestuff (e.g., methyl orange or methyl red). This dyestuff is oxidised and its intense colour is destroyed by the bromine, but only after the metal has been completely oxidised.

This method, details of which are given below, is highly recommended for arsenic, antimony and tin in ores and alloys.

**Arsenic or Antimony.** Prepare a decinormal solution of potassium bromate by dissolving 2.783 grm. of the salt (which should have been dried at 110° C.) in water and diluting to 1 litre. This solution should be standardised against a known weight of the metal to be determined. Thus, trivalent antimony is oxidised as follows :

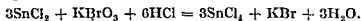


Dissolve an accurately-weighed quantity of about 0.2 gm. of finely-powdered antimony in 20 ml. of concentrated hydrochloric acid to which a few drops of bromine have been added. Use a covered beaker and warm the liquid, shaking it occasionally. When the metal has dissolved, remove the excess of bromine by evaporation, cool, and add cautiously about 1 gm. of sodium sulphite to reduce the antimony. Remove the excess of  $\text{SO}_2$  by evaporation. To do this, the volume of the liquid must be reduced by about one-half, and if any arsenic happens to be present it will necessarily be lost by volatilisation as chloride. Wash down the cover and the sides of the beaker with hot water. Add that volume of concentrated hydrochloric acid which is equal to one-quarter of the volume of the liquid already present, heat to  $80^\circ \text{C}$ ., and run in slightly less than the calculated quantity of bromate. Add 3 drops of methyl orange and continue to run in the bromate, slowly, with continual shaking, until the colour of the dye disappears. Wait one minute, and then add another drop of indicator to make quite sure that the end-point has been reached.

The percentage of antimony in an alloy, after the removal of interfering elements, can be determined by exactly the same process; so also can the quantity of antimony in a solution. In the latter case, reduction with  $\text{SO}_2$  may not be necessary.

The titration of trivalent arsenic follows the same lines as the antimony titration, although, for arsenic, the concentration of hydrochloric acid need not be so high.

**Tin. Method 1.** Place the solution, which should contain 0.15 to 0.2 gm. of tin and should be faintly acid with hydrochloric acid, in a 200-ml. conical flask. This flask should be fitted with a Bunsen valve (p. 142). To the cold solution add about 0.15 gm. of aluminium wire, which should have been cut into short lengths. When all the tin has been precipitated, add 50 ml. of 50 per cent. hydrochloric acid and heat gently until all the tin has dissolved. Slip off the rubber cap of the Bunsen valve and connect the glass tube at once to a Kipp apparatus which is producing  $\text{CO}_2$ . Cool in an atmosphere of carbon dioxide. Titrate with decinormal potassium bromate solution, using methyl orange as indicator.



**Method 2.** As in the first method, precipitate the tin with aluminium wire and then dissolve it in hydrochloric acid. A 500-ml. flask with a round bottom should be used for these operations. The flask should be tightly stoppered with a rubber bung, through which pass the stem of a separating-funnel and a second tube fitted with a stop-cock and with a Bunsen valve. Before dissolving the precipitated tin in hydrochloric acid, it is well to add a piece of magnesite to ensure that all air will be removed from the flask. When the tin and magnesite have dissolved and it is judged safe to do so, close the stop-cock of the second tube and cool the flask. A partial vacuum should be produced.

Place in the separating-funnel a solution containing a known volume of decinormal potassium bromate, in quantity more than sufficient to oxidise the tin; and potassium bromide in considerable excess over the residual bromate (0.5 to 1 gm. of  $\text{KBr}$ ). This solution should not contain

dissolved air. Open the stop-cock of the separating-funnel carefully and allow the bromate-bromide solution to mix with the solution of stannous chloride. The tin will be oxidised almost instantaneously by the liberated bromine, but, as the bromate was added in excess, some free bromine will still be present. This is determined by allowing it to react with potassium iodide and then titrating the liberated iodine with sodium thiosulphate, using starch as indicator. Transfer a solution containing about 0.5 grm. of potassium iodide from the separating-funnel into the flask. Wash down the funnel and the neck of the flask, and carry out the titration with a standard solution of sodium thiosulphate.

It is desirable to standardise the bromate solution by carrying out a parallel experiment using a known weight of pure tin.

**Arsenious Oxide as a Volumetric Reagent.** This reagent is of importance in the determination of "available" chlorine in bleaching-powder, of chlorine in aqueous solution, and of hypochlorites generally. As the titration is carried out in alkaline solution, chlorates do not interfere, and therefore the method is superior to the iodometric method (p. 170) for the evaluation of bleaching-powder.

The standard solution of arsenious oxide is prepared as described on p. 167.

**The Evaluation of Bleaching-powder, using Arsenious Oxide.** Prepare a suspension of the powder as described on p. 158. The indicator is potassium iodide-starch paper, used externally. This is prepared by making 1 grm. of "soluble starch" into a cream with water, and pouring this slowly into about 90 ml. of boiling distilled water. Boil gently for one minute, add a solution of 1 grm. of KI in a little water, cool and filter. Then soak strips of filter paper in the solution, and hang them up to dry in an uncontaminated atmosphere.

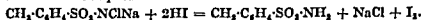
Run the arsenite solution, 5, 10, 15 . . . ml. at a time, into 25 ml. of the bleaching-powder suspension. After each addition, withdraw a drop on a glass rod and place them in orderly rows on the paper. If the end-point has not been reached, iodine will be liberated from the potassium iodide and this will give a blue stain with the starch. Having obtained a 5-ml. "bracket," proceed to make a 1-ml. "bracket," and then, on the third titration, find the end-point to within 0.2 ml. Finally, run into a fourth portion of the suspension that volume of standard arsenite solution, less 0.2 ml., which is required to reduce it completely, add a few drops of the potassium iodide-starch solution to the contents of the flask, and finish the titration.

#### Use of Choramine-T

The formula for this compound, which is readily obtainable pure, is



Its aqueous solution is reasonably stable, but it will react quantitatively with an acidified solution of potassium iodide as follows :



potassium iodide, in the presence of hydrochloric acid, and by titrating the liberated iodine with standard sodium thiosulphate, in the presence of starch ; or by running it from a burette into a known volume of standard arsenious solution (p. 167), in the presence of sodium bicarbonate. In the latter case, if a small crystal of potassium iodide and a little starch solution are added, the production of a permanent blue colour will mark the end-point.

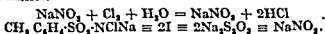
The determination of Tin by this reagent has already been described (p. 181).

#### Determination of Nitrites with Chloramine-T

The solution for analysis should contain 2 to 3 grm. of sodium nitrite, or an equivalent quantity of other nitrites, per litre.

To 25 ml. of the nitrite solution add 25 ml. (excess) of an approximately decinormal solution of chloramine-T, followed by a few millilitres of 10 per cent. acetic acid. Allow two minutes for the reaction to take place. Then add 10 per cent. potassium iodide solution and titrate with standard (approximately decinormal) sodium thiosulphate, using starch as indicator.

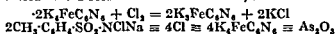
Titrate 25 ml. of the chloramine-T solution, under the same conditions with the sodium thiosulphate. The difference between the two volumes is a measure of the nitrite.



#### Determination of Ferrocyanides with Chloramine-T

water-bath to 40° C.

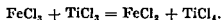
Determine the excess of chloramine-T by adding 20 ml. of a cold, saturated solution of sodium bicarbonate, a small crystal of potassium iodide and starch, and by titrating with standard sodium arsenite solution. Titrate a suitable volume of the chloramine-T solution with the arsenite, under the same conditions.



#### USE OF TITANOUS CHLORIDE SOLUTION AS A REDUCING AGENT

Titanous chloride is a reagent of great importance for the determination of ferric iron and, consequently in those determinations of oxidising agents which involve the use of ferrous sulphate. Thus, instead of back-titrating the excess of ferrous iron with a standard solution of another oxidising agent, the weight of ferric iron produced is determined with titanous chloride.

Titanous chloride reduces ferric salts as follows :



If a considerable quantity of ammonium thiocyanate is present in a solution of ferric chloride, that solution will be coloured a dark red. If a solution of titanous chloride is added the colour will fade, owing to the reduction of the ferric iron. Directly the titanous chloride is in excess all the iron is reduced, and the solution suddenly becomes almost colourless. Thus, ammonium thiocyanate can be used as an indicator without this reagent.

*Note.* This red colour is due to the presence of a complex ferric thiocyanate in solution. The undissociated salt is red; its ions are practically colourless. The converse is true of most other indicators. Therefore, although the general rule is that small quantities of indicators should be used in a dilute solution, a comparatively large and constant concentration of ammonium thiocyanate should be used in a comparatively concentrated solution.

**Preparation of Titanous Chloride Solution.** Titanous chloride is usually sold as a solution containing about 20 per cent. of the salt by weight. The volumetric reagent is prepared by taking a suitable volume of the concentrated solution in a flask, and by boiling it for a minute with twice its volume of concentrated hydrochloric acid. It is then diluted with water and placed in a storage bottle (Fig. 84), which it should fill to the neck.



An atmosphere of hydrogen is maintained over the titanous chloride (which is easily oxidised by the oxygen of the air) by means of the apparatus shown at A in the diagram. This consists of a glass tube some 8 inches in length and at least 1 inch in diameter. Some sticks of pure zinc are placed in the tube, and the bottom is closed by a cork through which a hole about 0.5 cm. in diameter has been bored. The glass tube is placed in a capacious glass cylinder. It is connected to the storage bottle, as is also the burette, in the manner indicated in Fig. 84.

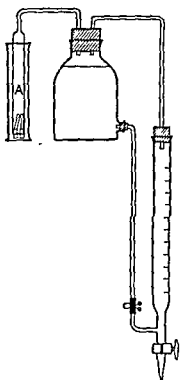


FIG. 84. STORAGE BOTTLE FOR TITANOUS CHLORIDE.

When the apparatus is set up and the bottle is filled to the neck with the solution of titanous chloride, hydrochloric acid diluted with its own volume of water is placed in the glass cylinder. When the burette stop-cock is opened to the air, the acid passes through the hole in the cork and reacts with the zinc. When this cock is closed, the hydrogen produced drives the acid back into the cylinder, and the action ceases. Pass a slow stream of hydrogen through the apparatus for several minutes to drive out all the air. The burette is filled by shutting the stop-cock and opening the clip on the side-tube.

*Note.* In some laboratories an electrolytic apparatus for the production of hydrogen is preferred to that described above. This has the advantage that there is no zinc or hydrochloric acid to be renewed, though such renewals are neither troublesome to make nor frequently required. A description of the electrolytic apparatus follows: At A, Fig. 84, there is a glass tube closed tightly at the top by a rubber bung through which passes a platinum wire. This wire is welded to the cathode which is preferably a piece of platinum foil about 6 inches square and bent into the form of a tube. The cathode should hang

the space is a nickel cylinder fitting between the inner tube and the outer glass connecting this apparatus with wool to return to A any of the battery supplying a current of 3 to 4 amps. at 12 to 16 volts should be connected permanently to the electrodes.

can be drawn off quickly without air entering through A. If much solution is used up in a short time, either the electrolytic hydrogen may not be produced quickly enough or the electrolyte will get very hot. In both cases the apparatus will fail.

A normal solution of titanous chloride contains 154.3 grm. of  $\text{TiCl}_3$  per litre. It is usual to work with solutions of either approximately 0.1 N. or approximately 0.02 N. concentration. Any calculations given in this

book are based on the assumption that the decinormal solution is being used.

*Note.* There are some reasons for preferring a solution of titanous sulphate to one of titanous chloride. The former is not so easily oxidised by the oxygen of the atmosphere; on the other hand, it is more easily hydrolysed and cannot be used in very dilute, weakly acid solutions.

**Standardisation of Titanous Chloride Solution.** In practice a solution of titanous chloride is rarely standardised directly, because it is used in such a way that a knowledge of the exact concentration in grammes per litre is unnecessary. An oxidising agent is allowed to react with a ferrous salt, and the ferric iron produced is titrated with the  $\text{TiCl}_3$ . A known volume of a standard solution of a ferric salt is then titrated with the  $\text{TiCl}_3$  under the same conditions as before. The ratio of the two volumes of  $\text{TiCl}_3$  is the ratio of the weights of ferric iron present in the two solutions. A suitable supply of a standard ferric salt is therefore necessary.

Prepare a considerable quantity of a solution of ferric ammonium alum containing about 40 gm. of the salt per litre, acidified with sulphuric acid to prevent hydrolysis, and standardise it against pure iron, or against pure crystals of ferrous ammonium sulphate. Accordingly, weigh out about 1 gm. of pure ferrous ammonium sulphate into a 500-ml. conical flask. Dissolve the crystals in a small quantity of water acidified with a little hydrochloric acid. Precipitate the iron as ferrous hydroxide by adding ammonia. Oxidise the ferrous hydroxide by adding a pure solution of hydrogen peroxide. Boil for ten minutes to decompose the excess of the peroxide. Up to this stage, the solution must be reasonably concentrated, certainly not more than 50 ml. in volume, or the destruction of the excess of hydrogen peroxide will be a lengthy process. The ferric hydroxide catalyses this decomposition. Then dissolve the ferric hydroxide in hydrochloric acid. A solution of ferric salt of accurately-known iron content is thus obtained.

Cool this solution and add water until the volume is about 100 ml. Add 10 ml. of a solution containing 100 gm. of  $\text{NH}_4\text{CNS}$  per litre from a pipette. Displace the air from the flask by a stream of  $\text{CO}_2$ . Then titrate with  $\text{TiCl}_3$  from the burette, keeping the stream of  $\text{CO}_2$  running until the end-point has been reached.

Take 50 ml. of the alum solution, acidify it further with hydrochloric acid, bring the volume to 100 ml., add 10 ml. of indicator and titrate it in turn with the  $\text{TiCl}_3$  under exactly the same conditions.

The arbitrary solution of ferric alum has now been standardised.

As it is almost impossible to prevent slight oxidation of the titanous chloride solution, its concentration will probably change slightly from day to day.

### Determination of Iron in an Ore by Titanous Chloride

Weigh out accurately about 2 gm. of the powdered ore and dissolve it in  $\text{HCl}$  as described on p. 149; make up the solution to 250 ml. Place 25 ml. of it in a conical flask, dilute to 100 ml. with water, add 10 ml. of  $\text{NH}_4\text{CNS}$  indicator, and titrate with the titanous chloride solution. All air must be displaced from the flask by carbon dioxide.

Determine the iron value of the titanous chloride by titrating 50 ml.

of the standard ferric alum solution (see above) with it under the same conditions. If the end-point of the first titration has been correctly reached, it suffices to run the ferric solution into the spent solution of the ore.

From the two titrations the percentage of ferric iron present in the ore can be calculated.

Take a fresh portion of 25 ml. of the ore solution. Oxidise the iron with hydrogen peroxide (p. 187) and repeat the titration. The total iron is now known, and the ferrous iron can be determined by difference.

### Determination of Tin by Titanous Chloride

The metal is dissolved in concentrated hydrochloric acid or, if in the form of a salt, in some suitable solvent. An aliquot portion of the solution is reduced with nickel foil, as has been described on p. 165.

The nickel foil is removed and washed with air-free distilled water before the solution is cooled. Then a considerable measured excess of the standard ferric alum solution is added to the hot solution of tin :



After 5 minutes, the contents of the flask are cooled, and the excess of iron is titrated with titanous chloride. The iron value of the latter solution is found by adding 50 ml. of the alum solution to the spent solution in the flask. The indicator is ammonium thiocyanate, and an atmosphere of carbon dioxide must be maintained during titration.

### Determination of Nitrates or Persulphates by Titanous Chloride

A suitable weight of the salt is allowed to react with a measured excess of an arbitrary solution of a ferrous salt, as described on pp. 151 and 160, respectively.

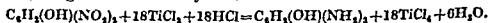
The solution is cooled and titrated at once with titanous chloride. The iron value of the titanous chloride is then found. Oxygen must be excluded. It is advisable to make up the partially oxidised ferrous solution to a known volume and to titrate an aliquot portion, because there will almost certainly be further oxidation of the excess of ferrous salt during this operation.

It is essential to run blanks in parallel with the assays, to obtain a correction for any ferric iron originally present in the ferrous solution and for any oxidation of the ferrous salt other than by the nitrate or persulphate.

### Determination of Picric Acid by Titanous Chloride

Titanous chloride can be used in the determination of many organic compounds, including numerous dyestuffs. Only one such example can be given here. Further information should be sought in *New Reduction Methods in Volumetric Analysis*, by Knecht and Hibbert.

The determination of picric acid is based on the fact that a large excess of titanous chloride reduces the nitro groups to amino groups. The excess of the reagent is then back-titrated with a standard solution of ferric alum, using ammonium thiocyanate as indicator.



Weigh out accurately about 1 gm. of picric acid, dissolve it in water, and make up the solution to 1 litre.

Put 50 ml. of the solution into a 500-ml. conical flask through which carbon dioxide is passing, through inlet and outlet tubes in the cork stopper. Add hydrochloric acid and 50 ml. of an approximately decinormal solution of titanous chloride. Boil for ten minutes. Cool. Add 10 ml. of ammonium thiocyanate indicator, and titrate with the standard solution of ferric alum.

Find the value of the titanous chloride in terms of iron by running a blank exactly as above, the picric acid being absent.

### Determination of Titanium

The titanium is reduced to the trivalent condition by passing an acidified solution of the element over zinc contained in a Jones reductor. The titanous salt passes into an excess of a solution of ferric alum, and this excess is back-titrated with titanous chloride solution; or the ferrous iron produced in the reaction is titrated with standard potassium permanganate. The former method possesses the great advantage that it can be used if the titanium solution itself contains iron.

**Determination of Titanium in Titanium Dioxide.** Weigh out accurately about 1 gm. of the sample of dioxide and fuse it in a nickel crucible with ten times its weight of potassium hydroxide until the melt is perfectly clear. Cool, and dissolve the mass in hot, dilute hydrochloric acid. Cool, and make up to 250 ml.

Activate the zinc of a Jones reductor (p. 148) with dilute hydrochloric acid, and place 100 ml. of a standard ferric solution of approximately decinormal concentration in the filter-bottle.

Take 50 ml. of the titanium solution, dilute to 150 ml. with water, and raise the hydrochloric acid content of this solution to about normal. Pass the liquid slowly through the reductor into the iron solution. Wash the zinc with dilute hydrochloric acid and distilled water. Add 10 ml. of the ammonium thiocyanate indicator and titrate the excess of iron at once, in an atmosphere of carbon dioxide, with arbitrary titanous chloride of approximately decinormal concentration. Let  $x$  ml. be the volume required.

Standardise the titanous chloride against 25 ml. of the ferric solution under exactly the same conditions. Let the volume of titanous chloride used be  $y$  ml. The weight of titanium in one-fifth of the dioxide equals the weight of titanium in  $(4y - x)$  ml. of the solution.

Alternatively, if the titanium dioxide contains no iron, the weight of the ferric salt-reduced by the titanium can be determined by titration with a standard solution of potassium permanganate of approximately decinormal concentration. In this case a blank assay should be run to ensure that no ferrous iron has been introduced from the zinc or from some other source.

**Note 1.** The reduction of the titanium in the Jones reductor may be slow. It can be hastened by heating the solutions to  $30^{\circ}\text{C}$ ., but in that case there will be large consumption of zinc. If care is taken, it is possible to reduce warm, sulphuric acid solutions of titanium quantitatively in the reductor.

*Note 2.*

solution,  
in which  
bottom of  
with a be  
fairly eas.

from the neck by platinum wire. Push the glass rod through the cork until the zinc is hanging in the liquid, and allow reduction to proceed for twenty to thirty minutes.

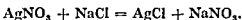
Raise the cork slightly and slip a delivery tube, through which pure carbon dioxide is passing, into the neck of the flask. The flask should be kept in free distilled water. Care not to allow the cork and its fitting to rise above the water. At the same time, titrate as soon as possible with titanous chloride, using ammonium thiocyanate as indicator.

## SECTION VIII

### UNCLASSIFIED VOLUMETRIC DETERMINATIONS

#### Determination of Silver by Standard Sodium Chloride Solution

WHEN a solution of silver nitrate, or other soluble silver salt, is mixed with a solution of sodium chloride, the silver is precipitated as the white insoluble chloride as follows :



Accordingly, the weight of silver present in a solution may be determined volumetrically by precipitating the chlorine from a known volume of NaCl solution of known concentration by means of the silver solution. Under certain conditions an indicator is unnecessary, because the presence of a turbidity caused by the addition of a few drops of one of the solutions to the other will show that the end-point has not been reached, and *vice versa*. However, potassium chromate, which gives a brick-red precipitate with an excess of silver nitrate, may be used, and several adsorption indicators are available.

**Determination of Silver without an Indicator.** It is preferable to add the salt solution to the silver solution ; free nitric acid must be present ; and the presence of a small quantity of pure barium nitrate is desirable. The doubly-charged positive barium ion aids the coagulation of the precipitate. As an exercise, determine the percentage of silver in pure silver nitrate as follows :

Weigh out accurately about 0.4 grm. of the silver nitrate into a well-stoppered, 200-ml. bottle. Add about 100 ml. of water, a few drops of concentrated nitric acid, and a small crystal of barium nitrate. Titrate with approximately decinormal, -standard sodium chloride solution (5.845 grm. per litre), by adding 20 ml. at once, stoppering the bottle, and shaking it vigorously until the precipitate of silver chloride has coagulated and settled, leaving a clear solution. The volume of sodium chloride taken should leave the silver still in excess. Continue to add the sodium chloride, 1 ml. at a time, stoppering and shaking after each addition, until the portion of sodium chloride fails to give a turbidity.

Repeat the determination, using a fresh portion of the sample of silver nitrate, and running in at once that volume of the sodium chloride solution, less 1 ml., which the first titration has indicated will be required ; and then adding the chloride 2 drops, or 0.1 ml., at a time.

This process is a modification of the Gay-Lussac-Stas process for the assay of silver. This is probably the most accurate volumetric determination known, as it enables the percentage of silver in bullion to be determined to 1 in 10,000 ; for further information, see Smith's *The Sampling and Assay of the Precious Metals*.

**Determination of Silver using an Adsorption Indicator.** The precipitate of silver halide, when it is first formed from a solution, is colloidal in nature, and the particles are charged. Whether this charge is positive or negative

apt to adsorb either soluble iodide or silver nitrate, as well as the chromate, that reasonable results can be obtained only in dilute solution and if the silver nitrate is added slowly, the vessel being stoppered and shaken after the addition of every 2 or 3 ml. of the silver nitrate.

It is essential when using this indicator that the solution be neutral, or only very weakly acidic. If it is alkaline, either a precipitate of silver oxide is formed or the silver salts are not precipitated. If it contains a strong acid, the potassium chromate is changed to potassium dichromate and, as silver dichromate is a soluble salt of no striking characteristics, the end-point is not shown.



To make an acidic solution neutral, add pure, precipitated chalk in such quantity that only a small weight of the chalk remains undissolved. To make an alkaline solution neutral, add nitric acid in slight excess, and neutralise the excess with precipitated chalk.

*Procedure.* Suppose that an approximately decinormal solution of silver nitrate is to be analysed. Prepare a suitable standard solution of silver nitrate by dissolving an accurately-weighed quantity of about 3.4 gm. of the pure crystals in water and diluting to 200 ml. Prepare also an arbitrary solution of sodium chloride containing about 6 gm. of the salt per litre.

Measure out 25 ml. of the chloride solution into a conical flask, or, better, in a porcelain evaporating-dish. The dish should stand on a mortar so that it remains steady when its contents are stirred. Add 2 drops of a 10 per cent. aqueous solution of potassium chromate. (If chloride is present in the chromate, add silver nitrate solution to the whole of the indicator solution until there is a permanent red precipitate, and filter.) Dilute the chloride solution to about 75 ml. and run in the silver nitrate from the burette, stirring or shaking constantly. Throughout most of the titration, the silver chloride is suspended in the liquid in a finely-divided state. Near the end-point a warning that the titration is nearly over is given by the sudden coagulation of the precipitate. Take the burette reading when a faint tinge of red persists in the liquid.

Transfer the silver solution to be analysed to a burette, and carry out a similar titration to the same intensity of colour, which must be remembered. It is no use putting aside the first vessel to serve as a standard, because the colour of the chromate will almost certainly change on standing.

Although there probably will be small indicator errors in each titration, yet, as the concentrations of the two solutions of silver nitrate are similar, these errors will be the same, and the ratio of the volumes of silver nitrate used will be a reliable measure of their relative concentrations.

### Determination of Chloride, Bromide or Iodide in Solution by Standard Silver Nitrate

The processes described above for the determination of silver by standard sodium chloride also serve for the determination of a chloride, bromide or iodide in solution by standard silver nitrate. It is convenient to use a decinormal solution of silver nitrate, made by dissolving 10.99 gm. of the salt in water and diluting to 1 litre. The use of phenosafranine as indicator

is strongly recommended for the determination of chlorides and that of eosin for bromides. However, owing to adsorption troubles iodides are best titrated with potassium iodate, using the iodine monochloride method (p. 180). Iodides in the presence of chlorides can be determined by silver nitrate, using rose bengal as adsorption indicator (p. 193). No volumetric method involving the use of silver nitrate is known which will serve to distinguish between bromide and chloride.

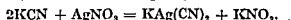
In the determination of bromides and particularly of iodides, it is better to standardise the solution of silver nitrate against standard solutions of potassium bromide and potassium iodide respectively, rather than to make it up by weighing.

*Note.* The silver in spent solutions or discarded precipitates from these analyses may be recovered as follows: Tip all the residues into a large jar, in which an excess of commercial silver chloride has been deposited on a fluted paper, wash it with water and filter the contents and ignite them in a large

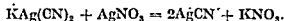
### Determination of Cyanide by means of Standard Silver Nitrate Solution

The solution of hydrocyanic acid, or soluble cyanide, is made alkaline by the addition of potassium hydroxide in excess, and a standard solution of silver nitrate is added. As soon as the silver solution is present in excess, a precipitate of silver cyanide is formed.

During this reaction a soluble, double cyanide of silver and potassium is produced at first, and therefore, no precipitate is formed:



As soon as more than sufficient silver solution has been added for the formation of the double cyanide, a precipitate of silver cyanide is produced:



The appearance of this precipitate indicates the end of the first stage of the reaction. At the conclusion of this stage, each millilitre of decinormal  $\text{AgNO}_3$  solution which has been added will correspond with 0.01302 gm. of KCN.

The solution in which the cyanide is to be determined should be diluted considerably with water before it is titrated in a conical flask in front of a black background.

For practice, determine the percentage of potassium cyanide in a commercial sample of that salt, by weighing out successive lots of about 0.3 gm., dissolving each separately in about 100 ml. of cold water, and titrating with standard, approximately decinormal silver nitrate. As the commercial salt is always alkaline, the addition of potassium hydroxide is unnecessary.

A solution of cyanide containing free ammonia (such as a cyanide solution which has been used for gold extraction) may be mixed with a few drops of potassium iodide solution. The first drop of silver solution which is added



excess of that required to form the double salt will produce a precipitate of yellow silver iodide, showing that the reaction is complete.

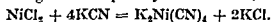
she . . . . . to be found, the acid  
sol . . . . . potassium hydroxide  
solution used should correspond as nearly as possible with that necessary for converting the acid into KCN, and precautions to prevent the loss of the volatile acid by evaporation must be taken.

Dilute hydrocyanic acid may be measured in an ordinary pipette, provided a plug of cotton-wool moistened with silver nitrate solution is pushed into the upper end of the pipette, since this liquid absorbs the vapour of the acid; concentrated solutions of the acid must always be weighed, using closed vessels. It is safer, when handling solutions of intermediate concentration, or even dilute solutions, to use a patent, self-filling pipette.

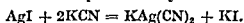
### Determination of Nickel by Potassium Cyanide

This method is both rapid and accurate, and is based on the following facts:

(a) Nickel, in the presence of a small excess of ammonia, reacts with potassium cyanide to give a complex cyanide:



(b) Silver iodide dissolves in potassium cyanide:



(c) Silver nitrate reacts with an excess of potassium cyanide to give the complex  $\text{KAg}(\text{CN})_2$ . Therefore, if a solution containing iodide and cyanide is titrated with silver nitrate, at first no precipitate is produced. Directly the silver present is more than equivalent to the cyanide present, a precipitate of silver iodide will be formed.

Three solutions are required:

(i.) A standard approximately decinormal solution of silver nitrate is made by dissolving the required weight of the pure, recrystallised salt in water and making up to a known volume.

(ii.) An arbitrary solution of potassium cyanide containing about 13.5 gm. of pure KCN and 5 gm. of pure KOH per litre. The potassium hydroxide increases the stability of the solution. Nevertheless, it is advisable to store this solution in a bottle connected to a burette, and to protect it from the carbon dioxide of the atmosphere by means of a soda-lime tube (see Fig. 78, p. 135).

(iii.) A solution of potassium iodide containing 20 gm. of the salt per litre.

**Standardisation of the Cyanide Solution.** A known volume, say 25 ml., of the potassium cyanide solution is run into a conical flask from a burette, and diluted to 150 ml. after the addition of 5 ml. of the iodide solution. The standard silver nitrate is then run in until there is a faint, but permanent, opalescence in the solution caused by the precipitation of silver iodide in a finely-divided form. A small known volume, say 0.3 ml., of the cyanide is added from the burette. The silver iodide should dissolve, and it is reprecipitated by 2 or 3 drops of silver nitrate. In this way the end-point can be found with great precision.

**Determination of Nickel.** For practice weigh out accurately about 5 gm. of nickel ammonium sulphate,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . Dissolve

the crystals in water acidified with a small quantity of dilute sulphuric acid and make up the solution to 250 ml.

Take 25 ml. of the nickel solution, dilute to 100 ml. and add ammonia until the liquid smells slightly of it. If a precipitate forms it will probably redissolve if a little ammonium chloride solution is added. Then add 5 ml. of the potassium iodide solution and a small, measured volume, say 0.5 ml., of the standard silver nitrate from a burette. The silver iodide produced should make the solution cloudy.

Titrate with the standard potassium cyanide solution until the cloudiness just disappears. This will take place when the KCN added is equivalent to the nickel in the solution plus the silver in the 0.5 ml. of the standard silver nitrate. Add  $\text{AgNO}_3$  cautiously, drop by drop, from the burette until the cloudiness due to the silver iodide reappears. Add the KCN until it just disappears again. Proceed in this way until the end-point has been ascertained exactly.

The equations on p. 190 show that one atom of nickel is equivalent to four molecules of KCN, and one atom of silver to two molecules of KCN. Or that

$$58.7 \text{ gm. Ni} \equiv 4 \times 65.1 \text{ gm. KCN.}$$

$$107.9 \text{ gm. Ag} \equiv 2 \times 65.1 \text{ gm. KCN.}$$

It has been shown experimentally that

$$x \text{ gm. Ni} + a \text{ gm. Ag} \equiv b \text{ gm. KCN.}$$

As the quantities  $a$  and  $b$  are known,  $x$  can be determined.

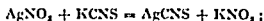
**Determination of Copper by Potassium Cyanide.** The method is the same as that described above for nickel.

is of a deep blue colour and the ammonia is a faint lavender, the dispensed with, and the copper solution titrated directly with standard cyanide solution. The sudden change in colour of the solution from blue to lavender marks the end-point (Mansfeld's method).

As the reaction between an ammoniacal solution of copper and potassium cyanide is not instantaneous, the results will be inaccurate.

### Determination of Silver by Potassium Thiocyanate

When a solution of silver in nitric acid is mixed with a solution of potassium thiocyanate, the silver is precipitated as white silver thiocyanate:



and if ferric sulphate has been previously added to the silver solution, the presence of thiocyanate in the slightest excess will be indicated by the distinct and permanent red colour of ferric thiocyanate. These reactions may be used for determining the proportion of silver present in silver alloys which have been dissolved in nitric acid.

An approximately decinormal solution of potassium or ammonium thiocyanate is prepared by weighing out about 10 gm. of the hygroscopic crystals, dissolving them in water and making up the solution to 1 litre. Sometimes it is preferable to use a solution of twice this concentration.

The indicator is prepared by boiling a saturated solution of ferric ammonium sulphate with a small quantity of nitric acid until all nitrous fumes have been expelled (Volhard's method).

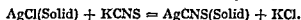
To Standardise the Thiocyanate Solution weigh out accurately about 0.25 grm. of pure silver. Dissolve it in 10 ml. of 1 : 1 nitric acid. Boil until all nitrous fumes have been expelled. Dilute to at least 100 ml. Add 2 ml. of the solution of ferric sulphate from a pipette, and titrate with the arbitrary thiocyanate solution until the solution becomes red. The solution must be stirred well during the titration. To ensure efficient mixing titrate in a stout conical flask fitted with a rubber bung. Near the end-point, stopper the flask and shake it vigorously.

For Practice, the percentage of silver in any silver alloy (such as a silver coin) may be determined. Any silver alloy may be used provided none of the other metals present colours the nitric acid solution strongly.

Weigh out accurately about 0.3 grm. of the silver alloy. Dissolve it in 15 ml. of 1 : 1 nitric acid, boil until no more nitrous fumes are evolved, and dilute the solution to 100 ml. with water. Add 2 ml. of the ferric solution as indicator, and allow the standard thiocyanate solution to flow in from a burette until a permanent, faint red tint is produced.

#### Indirect Determination of Chloride, Bromide or Iodide in Solution by Thiocyanate Solution

The solution of the halide is mixed with an excess of a decinormal solution of silver nitrate and the excess is titrated with thiocyanate which has been standardised against the silver nitrate. As silver chloride is more soluble than silver thiocyanate, the chloride must be removed by filtration before the end-point is reached. Consider a solution of sodium chloride to which an excess of silver



If the titration is carried out slowly enough, no permanent red colour will be produced until enough thiocyanate has been added to combine with all the silver

obtained.

The hydrochloric acid present in a solution may be determined as follows : Assume that the concentration of the acid is somewhat less than decinormal. Put 25 ml. of the acid into a stoppered bottle, together with 5 ml. of nitric acid, made by boiling 4 parts of the concentrated acid and 1 part of water until all nitrous fumes have been expelled. Add 25 ml. of decinormal silver nitrate. Stopper the bottle. Shake well. Filter. Wash the filter with water. Add to the filtrate and titrate with thiocyanate solution. If washing has not been sufficient, silver nitrate, say 5 per cent., corresponding with, say, 0.5 ml. of thiocyanate, will have been left on the paper and precipitate. In the second titration proceed

as before, but, before filtering, add that volume of thiocyanate which was required in the first titration. The excess of silver nitrate will now be small, and if one washing leaves 5 per cent. of it behind, the thiocyanate equivalent of this 5 per cent. will be very small. Thus it is necessary to wash the paper only two or three

only in acidic solutions and in the presence of the nitrate ion.

### Determination of Mercury by Thiocyanate

The method is similar to that for silver. The mercury must be in the mercuric state and the method fails in the presence of mercurous salts, chlorides and nitrous acid.



The solution for analysis should contain about 0.25 gm. of mercury as mercuric nitrate or sulphate. To it add 10 ml. of concentrated nitric acid or 5 ml. of sulphuric acid, and dilute to 100 ml. Destroy any reducing agent by adding potassium permanganate solution of reagent concentration (p. 518) drop by drop, until the colour of the permanganate persists for five minutes. Reduce the excess of permanganate with a minimum quantity of a solution of ferrous sulphate. Add 2 ml. of ferric indicator, and titrate with approximately decinormal potassium thiocyanate, as described under silver (p. 107).

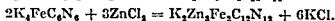
Standardise the thiocyanate solution against 0.25 gm. of pure mercury, which should be dissolved in hot, 50 per cent. by volume, nitric acid and treated with permanganate as has been described above.

The method works so smoothly that it is possible to use it to determine quantities of mercury of the order of 0.01 gm. In this case, use centinormal thiocyanate solution.

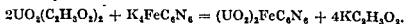
### Determination of Zinc by Potassium Ferrocyanide

**Determination by Ferrocyanide Solution.** When sufficient potassium ferrocyanide solution is added to an acid solution of zinc, the zinc is completely precipitated as a double ferrocyanide. In this reaction, the end-point may be indicated by the brown colour produced when the slightest excess of the soluble ferrocyanide is brought into contact with a solution of uranyl acetate, commonly known as uranium acetate. This indicator must be used externally.

The reaction between the zinc and the ferrocyanide depends on the conditions, and cannot be exactly represented by any equation. Most of the zinc is probably precipitated as  $\text{K}_2\text{Zn}_3\text{Fe}_2\text{C}_{12}\text{N}_{12}$ :



The equation representing the reaction between the uranium indicator and the ferrocyanide is:



The following solutions are required for the process :

(a) *The Standard Ferrocyanide Solution* is made by dissolving about 45 gm. of pure potassium ferrocyanide crystals,  $K_4FeC_6N_6 \cdot 3H_2O$ , in water, and making up the solution to 1 litre : each millilitre of this solution will correspond with approximately 0.01 gm. of zinc, its exact concentration being determined later by titration against the standard solution of zinc.

(b) *The Standard Zinc Solution* is prepared by dissolving 2.5 gm. of pure zinc in a little hydrochloric acid which has been diluted with its own volume of water, carefully avoiding loss by spitting. This solution is then made up to 250 ml. An alternative method consists in dissolving 11 gm. of pure  $ZnSO_4 \cdot 7H_2O$  crystals in water and making up the solution to 250 ml. Each millilitre of this solution contains 0.01 gm. of zinc. Precipitation of the zinc by hydrolysis can be prevented by adding a considerable quantity of ammonium chloride to the solution before making it up to a standard volume.

(c) *Uranyl Acetate*,  $UO_2(C_2H_3O_2)_2$ , in saturated solution.

*Standardise the Ferrocyanide Solution* (a) by introducing 25 ml. of the zinc solution (b) into a beaker of about 400 ml. capacity, adding 3 ml. of concentrated hydrochloric acid and 5 gm. of solid  $NH_4Cl$ , diluting to 250 ml., and heating to  $80^\circ C$ . Then add the ferrocyanide solution gradually from a burette, with constant stirring, until a brown coloration just appears when a drop of the liquid is mixed with a drop of the uranyl acetate solution on a white porcelain plate. The solution will now be below  $80^\circ C$ . It should be reheated to that temperature before finishing the titration. As the precipitation of the zinc is not immediate, it is necessary to continue the stirring of the solution for a minute or two, and then to test again with the indicator, more ferrocyanide solution being added, if necessary, until the brown coloration with the uranyl solution persists. The ferrocyanide reacts rapidly neither with the zinc nor with the uranyl acetate.

As an external indicator is in use, it is specially important to titrate by the method of "bracketing" (p. 141). Carry out the first two titrations rapidly, and do not be afraid of overshooting the end-point.

The volume of ferrocyanide solution equivalent to a definite weight of zinc is now known.

*The Determination* of the unknown quantity of zinc is carried out in exactly the same way as the standardisation of the ferrocyanide solution, the concentration of free hydrochloric present, the temperature of the liquid and the concentration of the ammonium chloride being similar. It is evident that the determination of zinc by this process cannot be made if other metals which form ferrocyanides insoluble in hydrochloric acid are present in solution. A nephelometric modification of the method is described on p. 308.

*Determination by Ferrocyanide using Diphenylbenzidine as an Oxidation-reduction Indicator.* The reduced form of this compound has a clear green colour ; the oxidised form is an intense purple. A solution containing

ferricyanide ions has an oxidising power strong enough to produce the purple colour, while the oxidised form is easily reduced by ferrocyanide ions. Whether the indicator is purple or green does not depend directly on the concentration of one or other of those ions, but on the ratio of their concentrations (pp. 139 and 214). If, therefore, a solution of zinc is titrated with a solution of potassium ferrocyanide containing a small quantity of potassium ferricyanide, at first the ferrocyanide ions will be removed as insoluble zinc ferrocyanide and the solution will be oxidising with respect to the indicator. Immediately all the zinc has been precipitated the ratio of ferrocyanide to ferricyanide ions will increase rapidly, the solution will reduce the indicator, and the intense purple colour will change to green.

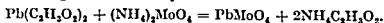
The solution of the indicator should be made by dissolving 1 gram. of diphenylbenzidine in 100 ml. of concentrated sulphuric acid. The method closely resembles the determination of zinc, using the external indicator, but the present solutions are not so concentrated. The optimum conditions are : the standard solution of zinc and solution to be analysed should have nearly the same concentration and should contain approximately 5 gram. of zinc per litre. Take 25 ml., add 10 gram. of ammonium chloride and 5 ml. of concentrated sulphuric acid. Dilute to 100 ml., add 5 drops of the indicator, and heat to 30° to 40° C. The indicator should be added to the cold solution. Titrate with a solution containing approximately 20 gram. of  $K_4FeC_6N_6 \cdot 3H_2O$  and 0.2 gram. of  $K_3FeC_6N_6$  per litre. The reagent should be added fairly slowly and at the same rates in the standardisation and in the determination.

The purple colour of the indicator often fails to develop until a considerable volume of the ferrocyanide-ferricyanide reagent has been added. On occasion it fails to appear at all, but the colour can then sometimes be produced by adding to the solution a small volume of some neutral zinc solution which has already been titrated and which has shown a satisfactory colour change. As the ferrocyanide requires an appreciable time for reaction with the zinc, towards the end of the titration the addition of a drop or two of the reagent will cause the solution to be temporarily reducing. The colour of the indicator will then be green, and the purple colour will return when a sufficient number of the ferrocyanide ions have been removed by precipitation. Titrate until the green colour remains for two minutes.

The indicator is very sensitive to working-conditions and will often fail to function in the presence of iron and of small quantities of oxidising and reducing agents. This method is therefore not suitable for zinc in alloys and ores.

#### Determination of Lead by Ammonium Molybdate

When Ammonium Molybdate Solution is added to a solution containing lead, the following reaction takes place :



The addition of excess of the molybdate will produce a yellowish-brown coloration with a solution of tannin. Solutions required :

(a) *Ammonium Molybdate Solution*, prepared by dissolving 9 gram. of pure ammonium molybdate in water and making up the solution to

1 litre. One millilitre will be approximately equivalent to 0.01 grm. of lead.

(b) *The Tannin Solution* used as indicator is prepared by dissolving 0.5 grm. of tannin in 100 ml. of water.

Since both these solutions are liable to undergo change, the former should be standardised at intervals of a fortnight and the latter should be frequently renewed.

(c) *Standardisation of the Ammonium Molybdate Solution.* Weigh out 0.3 grm. of pure lead assay foil, dissolve it in a little dilute nitric acid, and evaporate the solution considerably. Add a few millilitres of concentrated sulphuric acid and heat until white fumes are evolved. Dilute the cooled liquid with water to about 100 ml.; the lead will be precipitated completely as  $PbSO_4$ . Filter, wash the precipitate with 10 per cent.  $H_2SO_4$ , and then perforate the bottom of the filter-paper. Wash the precipitate completely into a small flask containing 5 to 10 grm. of solid ammonium acetate, using a fine stream of water from a wash-bottle. If some precipitate still adheres to the filter, the filter itself may be placed in the flask; the paper can be broken up and will then not affect the analysis. Boil the solution to dissolve the lead sulphate. Acidify with acetic acid, dilute to 200 ml., and boil again.

Titrate the nearly boiling liquid with the ammonium molybdate solution, continuing the addition of the reagent until a drop of the well-stirred liquid gives a faint yellowish colour with the tannin indicator, drops of which have been placed on a white tile. The yellow colour is not easily seen by ordinary artificial light.

For practice, commercial lead, a salt of lead, or a lead ore may be used. Weigh out from 0.5 to 2 grm. of the lead ore, according to the supposed lead content, dissolve it in nitric acid, using aqua regia if necessary, and evaporate the solution to a small bulk. Add a few millilitres of concentrated sulphuric acid and continue the evaporation until white fumes are freely given off. Add water, and boil in order to dissolve any anhydrous sulphates. Then cool, dilute with 100 ml. of water, filter, dissolve the lead sulphate in hot concentrated ammonium acetate solution, and titrate the hot solution, as is described above.

Note that as a considerable quantity, say 1 ml., of a decinormal solution of ammonium molybdate must be present in the titrated liquid before a recognisable colour is produced with the tannin, it is particularly important to use similar volumes of the molybdate solution in the standardisation and in the determination.

*Note.* When barium compounds are present in any quantity, they will interfere with the accuracy of the result. In this case dissolve the ore in  $HCl$  with the help of a little  $HNO_3$ , evaporate off the excess of acid, dilute considerably and precipitate the lead with  $H_2S$ . Filter off the  $PbS$ , wash it, and dissolve it in dilute  $HNO_3$ . Evaporate down with  $H_2SO_4$ , and proceed with the determination as is described above.

#### Determination of $P_2O_5$ in Soluble Phosphates by means of Uranyl Nitrate or Acetate

This process depends upon the fact that, when a solution of uranyl nitrate or of uranyl acetate and a solution of a phosphate are mixed together in the presence of an alkaline acetate and free acetic acid, the whole of the phosphate is thrown down as uranyl phosphate,  $UO_2HPO_4$ , or, if ammonia is present, as  $UO_2NH_4PO_4$ .

In carrying out the process volumetrically, the uranium solution is usually added from a burette to the solution of the phosphate, and the presence of an excess of the uranium solution is detected by the formation of a brown precipitate of uranyl ferrocyanide, when a drop of the mixed liquids is brought into contact with a drop of freshly-prepared potassium ferrocyanide solution (see p. 200).

*Standard* . . . . . out some 35 grm. of crystallised . . . . . 9 grm. of uranyl acetate  $[\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ , add 25 ml. of glacial acetic acid, dissolve the salt in water, and dilute the solution to 1 litre. If uranyl nitrate is used, also add sodium acetate to prevent the formation, under any conditions, of free nitric acid.

*The Standard Phosphate Solution.* Weigh out accurately 3.834 grm. of pure potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ . Dissolve this in water and dilute the solution to 1 litre. Fifty millilitres of this solution correspond with 0.1 grm. of  $\text{P}_2\text{O}_5$ .

*A Solution of Sodium Acetate containing Acetic Acid.* Dissolve approximately 100 grm. of sodium acetate in water, add 50 ml. of glacial acid, and dilute to 1 litre.

*A Solution of Potassium Ferrocyanide*, which must be freshly prepared.

*The Process of Titration.* Add 5 ml. of the sodium acetate solution and 1 ml. of a 10 per cent. solution of ammonia, which has been exactly neutralised with acetic acid, to 50 ml. of the potassium phosphate solution, and heat the liquid to  $90^\circ\text{C}$ . by placing the beaker on a hot plate or in a water-bath. Add the uranium solution from a burette, until a drop of the well-mixed liquids gives a faint reddish-brown coloration when it is brought into contact with a drop of the potassium ferrocyanide solution.

Heat the liquid once more to  $90^\circ\text{C}$ ., and again test a drop of it with ferrocyanide. If the brown coloration still appears, the titration has been completed. If, however, no coloration appears, continue to add the uranium solution until the brown colour is produced with the ferrocyanide after the liquid has stood for some time. The reaction between the uranyl salt and the phosphate is slow. In the final titration it is best to add most of the uranium solution rapidly, and to finish the titration by the slow addition of the remainder.

The above procedure indicates the method for phosphates in aqueous solution. Note that no results can be obtained if free mineral acid is present. Such acid must be replaced by acetic acid through the addition of a suitable quantity of sodium acetate. The conditions under which the actual analysis is carried out must resemble those of the standardisation as closely as possible with respect to quantities, concentration and temperature.

*Determination of Calcium and Magnesium Phosphates.* These phosphates cannot be correctly titrated with a uranium solution which has been standardised by means of potassium phosphate solution. The uranium solution which is used for the determination of  $\text{P}_2\text{O}_5$  in either of these phosphates must be standardised by a solution which contains 5 grm. of tricalcium phosphate per litre, in the manner described below.

Before this solution is prepared, the purity of the tricalcium phosphate standards must be tested by precipitating the phosphorus as ammonium

have been reached. Heat to  $90^\circ\text{C}$ . The solution should no longer react with the indicator. Complete the titration.

*Note.* If the phosphate solution is heated at the beginning of the titration calcium or magnesium phosphate may be precipitated, and it is redissolved in acetic acid only with much difficulty.



Determination of P. . . . . position, A substance of  
be determined by standard  
ely. The conditions which  
only be obtained by the  
when the solution to be determined is similar in all  
respects to the phosphate solution against which the uranium has been  
standardised. Moreover, the two titrations must be carried out under identical  
conditions. It is difficult rigidly to observe these points in practice. For this  
reason and because the recognition of the end-point by the external ferrocyanide  
indicator is not easy, the molybdate determination (p. 201) is the better of the  
two volumetric methods for phosphates, despite the fact that the uranyl acetate  
is the faster.

## PART IV

# MISCELLANEOUS METHODS OF ANALYSIS

## SECTION IX

### HYDROGEN ION CONCENTRATION POTENTIOMETRIC TITRATIONS

The measurement of hydrogen ion concentration and the determination of acids and alkalis, and of oxidising and reducing agents by the electro-metric (or, more accurately, potentiometric) method are now of the greatest importance.

When a bar of any metal is dipped into an aqueous solution of one of its salts, an equilibrium is set up. Some of the metallic ions in the solution may tend to deposit on the metal, when the electrode will become positively charged and the solution, as a whole, will be negatively charged. This tendency for the ions to deposit is governed by their osmotic pressure,  $p$ . On the other hand, the "solution potential,"  $P$ , which is the tendency for the metal to go into solution, may be so great that positive ions leave the electrode, when the electrode will be negatively charged and the solution positively charged. It can be shown that the difference in potential,  $E$ , between the metal and the solution is given by

$$E = \frac{RT}{nF} \log \frac{p}{P}$$

where  $n$  = valency of the ions,

$F$  = 96,500 coulombs (or 1 Faraday).

$R$  = gas constant,

$T$  = temperature in degrees absolute.

When values are substituted for these symbols, assuming a temperature of 18° C. and changing to common logarithms, the expression becomes

$$E = \frac{0.058}{n} \log \frac{p}{P}.$$

If two electrodes of the same metal are placed in two vessels containing solutions of different concentrations of the same salt of that metal, and these solutions are joined by a tube containing a solution of some suitable neutral salt (see *Note*), the combination will form an electric cell from which a small current can be taken. The E.M.F. of this cell is given by the algebraic difference of the potentials of the two electrodes; namely, by

$$E = E_2 - E_1 = \frac{0.058}{n} \log \frac{p_2}{P} - \frac{0.058}{n} \log \frac{p_1}{P} \\ = \frac{0.058}{n} \log \frac{p_2}{p_1}.$$

For dilute solutions, the osmotic pressure can be taken to be proportional to the concentration, so that the expression can be written

$$E = \frac{0.058}{n} \log \frac{C_2}{C_1},$$

where  $C_1$  and  $C_2$  are the concentrations of the metallic ion in the two solutions.

A piece of platinum coated with platinum black and immersed in gaseous hydrogen acts as if the electrode consisted solely of "metallic hydrogen." Platinum so treated is known as a hydrogen electrode. If one hydrogen electrode is dipped into a solution containing unit concentration of hydrogen ions and a second into a solution of unknown concentration,  $C$ , the two being connected as before, the E.M.F. developed is given by

$$E = 0.058 \log \frac{1}{C} = 0.058 P_H.$$

The expression  $\log \frac{1}{C}$  is widely used to characterise the hydrogen ion concentration, and, as the equations indicate, it is written  $P_H$ . The arithmetical convenience of the  $P_H$  notation will be obvious.

The above equation shows that, by measuring the E.M.F. of a cell absolutely, the hydrogen ion concentration can be measured exactly. The absolute measurement, though simple in itself, requires the use of a somewhat complex apparatus, which cannot be described here. For a suitable monograph on the subject, see p. 518. How the change in E.M.F. can be followed when a solution containing a base is titrated with an acid, will be described later.

*Note.* If two solutions of hydrochloric acid of different concentration are brought together without mixing, the hydrogen ions and chlorine ions will migrate independently across the boundary. As the hydrogen ion moves the faster, the more concentrated solution will soon contain an excess of negatively charged chlorine ions, and *vice versa*. A difference in potential will therefore exist at the liquid junction. The same will be true for any two salt solutions of different concentration, unless the two ions of the salt migrate at the same speed. It is obviously undesirable to have this effect at the junction of the tube and the solution. Therefore the salt solution in the connecting tube or bridge must give ions of the same mobilities. One of the few suitable salts is potassium chloride.

**Measurement of  $P_H$  by Indicators.** Provided that the solution to be examined contains no substance which reacts with or adsorbs the indicator and is not coloured in such a way that the tint of the indicator is interfered with, indicators can be used for the rapid and accurate determination of the  $P_H$  value. Such indicators must have been standardised against solutions of  $P_H$  and their effective ranges determined; suitable details are given in the Table on p. 495. A short account of this method for the measurement of the  $P_H$  of water is given on p. 237; with other types of sample it may be necessary to ascertain which of the indicators specified in the Table on p. 495 best covers the  $P_H$  range involved, and in such cases the universal indicator given on p. 495 should first be used to obtain an approximate  $P_H$  value. Further information must be sought in Clark's *Determination of Hydrogen Ions*.

**Buffer Solutions** may be defined as solutions having a definite  $P_H$ , which is not changed by the addition of even considerable quantities of other compounds.

A dilute solution of sodium hydroxide is said to be "unbuffered." It will have a definite  $P_H$ , but the accidental introduction of traces of other compounds from the container or from the air will change the  $P_H$ . It is therefore useless as a standard of hydrogen ion concentration. On the other hand, a solution of the salt of a strong base with a weak acid, such as sodium acetate, is hydrolysed by water, and the resulting solution is not neutral, but alkaline.



Provided the sodium acetate is in large excess, the addition of hydriions in the form of hydrochloric acid will have little or no effect on the  $P_H$ . The hydriion removes the excess of hydroxyl ion from the solution, thus upsetting the equilibrium shown above. More of the salt reacts with the water to produce a further supply of the hydroxyl ion, and the  $P_H$  remains constant. Sodium acetate is a typical buffer, but acts only in the one direction. If some free acetic acid is added to the solution of sodium acetate, the addition of a small quantity of sodium hydroxide will have no very great effect on the  $P_H$ . The solution now fails to respond materially to the addition of either acids and bases, and it is buffered in both directions.

Instructions for preparing more efficient buffer solutions than sodium acetate-acetic acid mixtures, are given below (see also Table on p. 495).

Potassium hydrogen orthophthalate is made as follows: Take 60 grm. of pure potassium hydroxide and dissolve in 400 ml. of water. Add 50 grm. of resublimed orthophthalic anhydride. Cool, and withdraw a portion of the solution, testing it with phenolphthalein. If it is not acid, make the solution slightly acid to this indicator by adding further small weighed quantities of

be recrystallised and dried carefully before use. Sodium hydroxide free from carbonate should be used.

Buffer solutions stored in sealed glass tubes of good quality may keep for long periods, especially if 1 drop of toluene be added to each before sealing. The more acid the solution, the more rapidly does it deteriorate.

**Exercises on Measurement of  $P_H$ .** Make up a series of buffer solutions of range  $P_H$  4.4 to 6.0 (Table on p. 495). Prepare solutions of sodium hydroxide and acetic acid of equal normality (about decinormal), titrating them against each other with phenolphthalein as indicator, and adding water to the more concentrated until they are in exact balance. To portions of 20 ml. of the acetic acid add 10, 12, 14 ml. of the sodium hydroxide. Place 20 ml. of these solutions and 20 ml. of the buffer solutions in a series of Nessler tubes (p. 235). Estimate their  $P_H$  by adding 10 drops of a 0.02 per cent. solution of methyl red to the contents of all the tubes. Stir, and match the colours.

Measure the hydrogen ion concentration of a decinormal solution of ammonium chloride, and that of tap-water.

**Drop-Ratio Method.** This method is included here because for most purposes it is sufficiently accurate, and, as it avoids the necessity for the preparation of buffer solutions, it is very convenient and rapid. Nine pairs of similar test-tubes, marked at 5 ml., are placed in a double-row test-tube rack (as indicated in Fig. 85). In those of the front row are placed 1, 2, 3 . . . 9 drops of the indicator solution in order, and to their respective partners in the back row are added 9, 8, 7 . . . 1 drop. One drop of 0.2 per cent. sodium hydroxide solution (2 drops for thymol blue) is then added to each tube in the front row, and 1 drop of 0.05 N. hydrochloric acid (1 ml. for bromophenol blue and 1 drop of 2 per cent potassium dihydrogen phosphate solution for the alkaline range of thymol blue) to each tube in the back row. The contents of each tube are then diluted to 5 ml. If each pair is viewed so that the light passes through both tubes, then at one end the extreme acid colour of the indicator is seen, while the other end corresponds with the extreme alkaline colour, and in between is a gradation of colours from one to the other. Each pair of tubes, therefore, corresponds in colour with one-seventh of the total pH range of the indicator. Thus, with bromophenol red the two extremes of the range represent  $P_H$  5.4 and 7.0, and the seven intermediate tubes with steps of approximately 0.2  $P_H$ . The test solution should, of course, be contained in a similar pair of tubes, each of which should contain 5 drops of indicator in a total of 5 ml. of liquid.

For practice, apply this method to a sample of tap water, and compare the results with those obtained by the method described above.

9	8	7	6	5	4	3	2	1
1	2	3	4	5	6	7	8	9
5.4	5.6	5.8	6.0	6.2	6.4	6.6	6.8	7.0
Acid colour.				Neutral colour.				Alkaline colour.

Top Row—Drops of acid bromophenol blue.

Bottom Row—Drops of alkaline bromophenol blue.

FIG. 85.—DROP-RATIO METHOD.

**Titration Curves.** The absolute measurement of the  $P_H$  by the electro-metric method requires considerable apparatus which has to be kept in condition, but the changes in  $P_H$ , for example during the titration of an acid with a base, can be followed much more easily. As, fortunately, these changes are frequently greatest at the end-point of a reaction, it is often sufficient to follow them only. As an example, consider the titration of 100 ml. of 0.1 N. HCl with 0.1 N. NaOH. The  $P_H$  of the original solution may be taken as unity. The addition of 90 ml. of NaOH and 10 ml. of water reduces the acid to 0.005 N. and a  $P_H$  of nearly 2.3; the addition of a further 9 ml. of NaOH changes the  $P_H$  to about 3.3; and so on, until, when equivalent volumes of acid and alkali are present, the solution is neutral with a  $P_H$  of about 7. Thus, the last 0.1 millilitre of NaOH changes the  $P_H$  by about 3.7 units. As the end-point is approached and passed therefore, there is a rapid change in  $P_H$ . To determine the end-point, it is therefore sufficient to recognise where the slope of the titration curve is changing most rapidly (see p. 218).

The hydrogen ion concentration ( $C$ ) of a solution is related to the E.M.F. of the cell:

Hydrogen electrode | the solution | normal solution of hydrogen ions | hydrogen electrode  
by the equation (p. 206)

$$E = 0.058 \log \frac{1}{C}$$

But, as the  $P_H$  is  $\log \frac{1}{C}$ , the E.M.F. also changes rapidly as the titration reaches completion, and the end-point can be determined by following this change. This method possesses certain advantages over the usual volumetric methods. It is independent of the "personal equation," as no colours have to be watched, and titrations can be carried out in solutions containing natural colouring matters and even in the presence of suspended solids. When neutralisation occurs in two steps, these stages are often marked on the curve. The neutralisation of orthophosphoric acid by

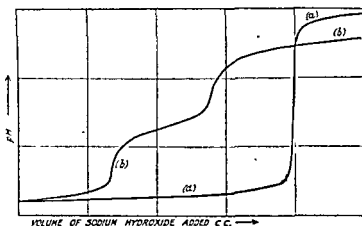


FIG. 86. TYPICAL TITRATION CURVES.

sodium hydroxide and of a solution containing a strong and a weak base by hydrochloric acid are examples of stepped reactions. Typical titration curves are reproduced in Fig. 86. Curve (a) represents the neutralisation of 0.1 N. HCl by 0.1 N. NaOH, and curve (b) the neutralisation of 0.1 N. phosphoric acid by 0.1 N. NaOH. In the latter curve the lower step corresponds with the formation of  $\text{NaH}_2\text{PO}_4$  ( $P_H$  5.0), the latter with that of  $\text{Na}_2\text{HPO}_4$  ( $P_H$  9.2).

**Apparatus for Determination of  $P_H$ .** A simple form of apparatus is shown in Figs. 87 and 88. Instead of a normal hydrogen electrode (a hydrogen electrode immersed in a solution containing 1.008 gm. of hydron per litre, p. 206), it is much more convenient to use as reference electrode a calomel electrode, the potential of which is some 0.283 volt higher than that of the hydrogen electrode. This difference does not affect the relative changes in E.M.F.

together on the steel with a flat  
leaving a tongue of metal when  
the two ends together in a smr

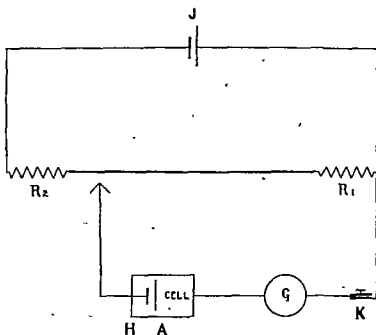


FIG. 87. GENERAL ARRANGEMENT OF ELECTROMETRIC APPARATUS.

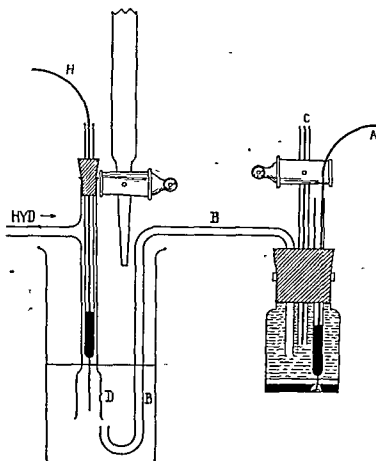


FIG. 88. TITRATION VESSEL AND CALOMEL ELECTRODE.

the tongue joins the foil should be avoided. Take a piece of soft, lead-free glass tube and draw it off to a thin point. Break off the tip and slip in the platinum wire until the foil touches the glass. Rotate the junction in a small, hot flame until the glass fuses to the top of the foil and the joint is tight.

Clean the foil by abrasion with fine emery-paper, wash it in alcohol-sodium hydroxide mixture, and finally, after leaving it for five minutes in chromic-sulphuric mixture, in distilled water. Do not subsequently touch the platinum with the fingers.

The foil has now to be coated with platinum-black. Take two small weighing-bottles. In one, place a 10 per cent. solution of sulphuric acid, in the other a 3 per cent. solution of platinic chloride acidified with a little hydrochloric acid. Suspend the electrode in the second vessel and electrolyse, using one lead accumulator, and a platinum wire as the anode. This wire should be held in the hand, and moved about in the solution. The foil should be covered with a black layer of uniform thickness, and the action should be stopped immediately the glint of the bright platinum can no longer be seen. Wash quickly under running water, transfer to the sulphuric acid, and electrolyse with a potential difference of 4 volts, until the "black" is thoroughly charged with hydrogen and the gas is streaming uniformly from the surface. If there are any dead spots, the electrode is probably useless, and the "black" should be removed by making the electrode the anode in a cell containing 1 : 1 HCl and electrolysing as before. The foil should then be ready for recoating with the platinum black.

Electrodes may be used again and again, provided they are kept scrupulously clean and are never allowed to dry. It is well occasionally to remove the platinum black by electrolysis and to recoat as described above.

Electrical connection is made to the platinum black by filling the tube in which it is sealed with mercury, and by poking an amalgamated copper wire into the mercury.

A hydrogen electrode made from platinum wire serves fully as well as the foil-electrode for many purposes. It is less easy to break and more easily repaired, but it must be reblacked more frequently than the foil. A wire is prepared for use as follows: Abrade with emery-paper. Rub with cotton-wool soaked in alcohol, taking care to leave no hairs on the wire. Raise the tip of the wire to a white heat in an alcohol lamp. Dip the tip in a solution containing 50 per cent. HCl, using the platinum black and "gas".

It is essential that the hydrogen used be pure. It is best prepared by the electrolysis of a 20 per cent. solution of potassium hydroxide in the electrolytic apparatus described on p. 186. For ordinary work, no purification of this hydrogen is necessary, except that great care must be taken to remove any potassium hydroxide carried in the gas by passing the stream through a long, vertical plug of glass-wool or through a wash-bottle containing water.

An easily-made Calomel Electrode is shown in Fig. 88. A layer of pure mercury is placed on the bottom of a bottle of diameter some 4 cm. and height from bottom to shoulder of 4 cm. Calomel paste, made by rubbing together calomel, mercury, and some of the potassium chloride solution in a mortar

13 (diameter, about 2 mm.) should be filled with solution. The calomel electrode

ele  
ele



the end of this sheath in such a position that bubbles of hydrogen can escape

The potentiometer circuit is arranged as shown in Fig. 87. In the sub-circuit the positive calomel a galvanometer  $G$ ,

hydroxide. The original  $P_H$  may be taken as unity and the original E.M.F. of the cell will be about 0.3 volt. Suppose the final  $P_H$  is 10. The final E.M.F. will be less than 1 volt. Then if  $R_1 : x : R_2 = 0.3 : 0.7 : 1$ , where  $x$  is the resistance of the potentiometer wire, the full potentiometer scale will be in use.

Neither the galvanometer nor the potentiometer need be of the best quality. A robust milliammeter of the pointer type, of internal resistance about 10 ohms and sensitivity 5 mm. per micro-ampere, is suitable. The zero mark should be at the centre of the scale. A rotary potentiometer having a total resistance of 75 ohms and a graduated scale some 30 cm. in length can be used.

**Titration of a Solution of Sodium Hydroxide of approximately decinormal concentration with 0.1 N. HCl.**

Set up the apparatus, and place 40 ml. of the alkali in the titration vessel, diluting it, if necessary, in order to cover the electrode. Pass in the hydrogen rapidly for three minutes. Stop down the gas stream and adjust the potentiometer, a point is found for which :

one minute and take a second reading. Continue until two consecutive readings agree. Run in 10 ml. of HCl from the burette. Mix by swirling the liquid round the beaker. Wait half a minute. Take the reading. Carry on in this way till the sudden increase in E.M.F. has been obtained. If the approximate end-point is known, add quantities of 1 ml. towards the end of the titration. The first titration gives a close approximation to the end-point. Repeat, carrying out the experiment a third time if necessary, adding smaller volumes of acid in the region of the end-point. Note that in electrometric titrations it is advisable to know the shape of the curve in its early and late stages. For example, suppose the end-point is at 38.5 ml. of HCl. The first titration shows it is between 30 and 40 ml. and nearer to 40 ml. The second titration should be made in the following steps : 0, 15, 25, 30, 33, 35, 36, 37, 38, 39, 40, 45 ml., and shows that the end-point is between 38 and 39 ml. Repeat, omitting any unessential stages up to 38 ml., and proceed 38.0, 38.2, 38.4, till past the end-point. The curve relating the potentiometer reading in cm. and the ml. of HCl added will then show the result correct to 0.05 ml. (Note 2.)

Note that it is preferable to run the acid into the alkali, because a faulty electrode may work perfectly in solutions of low  $P_H$  and may not break down until the solution is alkaline. It is well to discover the fault as soon as possible.

Titrate the sodium hydroxide with the hydrochloric acid in the usual way, using methyl orange or methyl red as indicator, and compare your results.

**Note 1.** In electrometric titrations, success can be more easily attained if work is carried out systematically. The titrating liquid should be run into the flask in a standard way during each addition, the burette read at the same relative time after each addition, the flask shaken for a definite time before the potentiometer is read, and so on. In short, use "drill movements."

It will be found that the E.M.F. of the cell depends somewhat on the position of the solution in the sheath. This variation is of no importance except when the absolute  $P_{\text{H}}$  of the solution is to be determined, but the potentiometer reading should be taken either just before or just after the escape of a bubble of hydrogen.

**Note 2** If the end-point cannot be read accurately from the curve, the following device may be of assistance

Instead of plotting  $\frac{dR}{dV}$  against the volume of NaOH added, where  $dR$  is the change in  $R$  produced by the addition of a small volume  $dV$  of NaOH, the ratio  $\frac{dR}{dV}$  is plotted against the total volume of NaOH added ( $V$ ) as in Fig. 89. Now we know that, as the end-point is approached, the change in  $R$  ( $dR$ ) increases considerably for only small additions of NaOH; consequently the above ratio (which incidentally, measures the angle between the horizontal and a tangent to the titration curve drawn at the point corresponding with the value of  $V$  in question) also increases. At the end-point it is a maximum, and if the titration is carried beyond this stage, a curve of the type shown in Fig. 89 results. It is apparent that it is possible in this way to deduce the end-point in cases where the readings available result in an appreciable gap between the two arms of the curve at the maximum; thus corresponds with a titration curve having an indefinite change of slope at the end-point. Since NaOH and HCl, however, are strong electrolytes, a sharp maximum should be obtained.

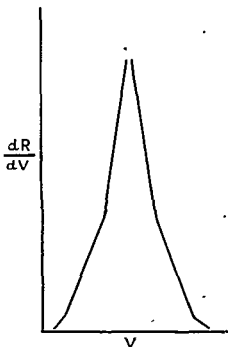


FIG. 89.

**Other Exercises.** Make up a standard solution of disodium hydrogen phosphate of approximately decinormal concentration and titrate it with standard hydrochloric acid.

Titrate sodium carbonate with hydrochloric acid.

Determine the temporary and permanent hardness of tap-water (p. 365), using the electric apparatus in place of the usual indicators.

Plot curves in all cases.

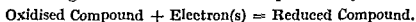
**Simplified Potentiometry (Pinkhof's Method).** This method provides an instructive exercise, particularly where the amount of apparatus available is limited; it also has practical applications in routine analysis. It depends on the fact that no potential exists between two similar electrodes in solutions

meter, a 100-ohms resistance and a tapping key, and add 0.05 N. NaOH to the acid from a burette. After each addition depress the tapping key momentarily; the neutralisation point is reached when little or no deflection occurs.

### Oxidation and Reduction Reactions

Electrometric methods are of great and increasing use in volumetric analyses which involve oxidation and reduction, particularly when a large number of similar determinations are to be carried out. The apparatus used is the same as that shown in Figs. 87 and 88, except that it is simplified by replacing the hydrogen electrode by a bright platinum electrode made by fusing a platinum wire into a glass tube. The platinum electrode is the positive pole of the titration cell. There is also no necessity to maintain a hydrogen atmosphere, and an open vessel can be employed, except in those cases where the reducing agent is easily oxidised by atmospheric oxygen. The vessels and platinum electrode must be kept scrupulously clean, the electrode as described on p. 211, and finally by heating it to a red heat in an alcohol flame.

The theory of the method is analogous to the theory of the hydrogen electrode. The general oxidation-reduction equation may be written :



An oxidising agent tends to gain electrons and, therefore, if a piece of platinum is placed in a solution of an oxidising agent, electrons will pass from the solid to the liquid, leaving the platinum positively charged and

between the electrode and the solution is given by :

$$E = E_0 + \frac{RT}{nF} \log \frac{\text{Concentration of Oxidised Form}}{\text{Concentration of Reduced Form}}$$

In this equation,  $E_0$  is a constant which will be equal to  $E$  when the concentrations of the oxidising and reducing forms are the same.  $E_0$  is known as the standard oxidation-reduction potential of the system.

The other symbols have their usual meanings (p. 205). When numerical values are substituted in the equation, the following relationship is obtained at 18° C. :

$$E = E_0 + \frac{0.058}{n} \log \frac{\text{conc. of "ic" form}}{\text{conc. of "ous" form}}$$

For the ferrous-ferric system,  $E_0$  is about 0.77 volt, and  $n$  is 1. The cell

Pt	Solution containing 5.6 gm. Fe <sup>+++</sup> and 5.6 gm. Fe <sup>++</sup> per litre	Salt Bridge	Normal Calomel Electrode
----	---	----------------	--------------------------------

will give an E.M.F., not of 0.77 volt, but of  $(0.77 - 0.283) = 0.487$  volt, the correction being necessary because the above standard of  $E_0$  is with respect to the normal hydrogen electrode, and a calomel electrode is now in use. If the ferric salt is reduced so that 1.02 gm. of ferric iron is left in a litre of the solution,  $E$  will become 0.432 volt. When 0.11 gm. is left,  $E$  will be 0.374 volt; when 0.01 gm. is left,  $E$  will be 0.316 volt, and so on. That is to say, toward the end of a titration, when the ratio of the concentrations of the two forms is changing rapidly, there will also

be a rapid change in the E.M.F. The above statement is equally true for oxidation.

The standard electrode potential, referred to the normal calomel electrode for the stannous-stannic system is  $-0.43$  volt, and the E.M.F. of such a cell is given by

$$E = -0.43 + \frac{0.058}{2} \log \frac{\text{conc. "ic" form}}{\text{conc. "ous" form}}$$

The E.M.F. of this cell will vary with varying stannous-stannic ratios much in the same way as that of the iron cell.

If a solution of ferric chloride is titated with stannous chloride, it follows from the equations that

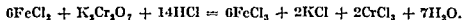
$$\frac{\text{conc. stannic}}{\text{conc. stannous}} = 10^{18}, \text{ and } \frac{\text{conc. ferric}}{\text{conc. ferrous}} = 10^{-8.5}$$

when the E.M.F. of the cell is zero.

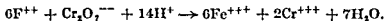
If two equivalents of stannous chloride are added progressively to one equivalent of ferric chloride, the E.M.F. of the cell will at first be high. It will fall suddenly on the addition of a few drops of the stannous solution, but will be near  $0.49 \pm 0.1$  volt until nearly one equivalent of stannous chloride has been added. It will again fall very suddenly and steeply, but, after the addition of one equivalent plus a few drops of stannous chloride, it will again flatten out and will remain in the range  $-0.3$  to  $-0.43$  volt while the second equivalent is being added. The intermediate and final parts of the curve, in fact, will closely resemble the sodium hydroxide-hydrochloric acid curve (*a* in Fig. 80, p. 209), and it will be equally easy to determine the end-point.

Note that the equations show that the E.M.F. is dependent only on the ratio of the concentrations, not on the absolute concentration. The titration curve should be independent of the initial concentration, provided the solutions are so dilute that they are completely ionised; or, rather, that the activities of the ions do not change on further dilution. It should be just as sharp in a millinormal as in a normal solution. Experimental difficulties, of course, do arise when working at extreme dilutions, but the electrometric method is capable of giving more accurate results in very dilute solution than are the ordinary methods.

Consider the oxidation of ferrous iron in hydrochloric acid solution by potassium dichromate:



Writing this equation in ionic form and neglecting ions which appear on both sides:



By choosing suitable conditions, namely, a large excess of hydrochloric acid (which keeps the hydron concentration practically unchanged throughout), and a dilute solution (so that the water concentration may be regarded as constant), the change in the E.M.F. of the cell can be made to depend on the concentrations of only four ions, namely,  $\text{Fe}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Fe}^{+++}$  and  $\text{Cr}_2\text{O}_7^{--}$ . The system can be divided into two, a ferrous-ferric and a chromium-dichromate system, and the E.M.F. curve for the titration of ferrous iron with potassium dichromate will closely resemble that for the titration of ferric iron with stannous chloride. Throughout

a titration, the concentration of the ferrous ion decreases slowly and those of the ferric and chromium ions increase slowly and regularly. The concentration of the dichromate ion, on the other hand, is exceedingly small until the end-point is reached. After the end-point, the concentrations of the first three ions may be regarded as constant, while there is an abrupt change in the concentration of the dichromate ion. This will be accompanied by an abrupt change in the rate of change of the E.M.F. of the cell.

The theory is given with a view to emphasising two points: (a) The method can be used in the titration of very dilute solutions; (b) the conditions of the experiment must be studied carefully.

**For Practice,** make up solutions of ferrous sulphate and potassium dichromate of approximately decinormal concentration. Standardise the iron solution against the dichromate in the usual way with potassium ferricyanide as external indicator (p. 149).

Take 20 ml. of the ferrous solution in a 800-ml. beaker. Add a mixture of 80 ml. of concentrated hydrochloric acid and 200 ml. of water, and mix well by swirling the beaker round on the surface of the bench. Titrate with the dichromate solution, adding this reagent 5 ml. at a time. Mix well, and wait a few seconds after each addition before reading the potentiometer. Plot the curve obtained.

Make any necessary alterations in the ballast resistances,  $R_1$  and  $R_2$ , and repeat, adding the reagent in volumes of 1 ml. when near the end-point. Carry out a third titration, determining a few early points and a few late points to give the general direction of the curve, and adding the dichromate in volumes of 0.2 ml. when near the end-point. The volume of reagent added should never be smaller than 0.2 ml. If well-spaced points are thus obtained, the end-point can be determined from the curve correct to 0.05 ml.

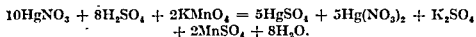
Dilute the ferrous and dichromate solutions 10 times and 100 times, and repeat the titrations. Compare the end-points obtained and the shapes of the curves. Compare also the electrometric and volumetric end-points.

*Note.* In very dilute solution an appreciable proportion of the ferrous salt may be oxidised by the air. Such solutions should be prepared from boiled, distilled water, and should be kept in stoppered flasks. A successful titration can be carried through only if the apparatus is absolutely free from grease and the platinum point is spotlessly clean.

**Determination of Iron in Commercial Aluminium.** Commercial aluminium may contain about 0.5 per cent. of iron. The sample should be freed from grease by washing it successively in ether, alcohol, and distilled water. Dissolve 1 gm. of the metal in 20 ml. of concentrated HCl and 40 ml. of water, in the 800-ml. beaker in which the titration is to be carried out. Cover with a clock-glass and warm gently. The reaction may be difficult to start, and difficult to control when it has started. When the aluminium has dissolved, boil the liquid for five minutes, keeping the beaker covered. Some samples of aluminium contain so much silicon that a clear solution will not be obtained. The presence of this silicon does not interfere. Add 30 ml. of concentrated HCl and 200 ml. of water, and immediately titrate with standard potassium dichromate solution

containing about 0.5 grm. of the salt per litre. The curve is not nearly so sharp as that obtained when a pure ferrous salt is titrated, but the method is probably the most accurate yet available. The dichromate is best standardised against a fresh solution of ferrous ammonium sulphate, using the electrometric method.

**Determination of Manganese in Steel.** Dissolve 1 grm. of the steel in 50 ml. of nitric acid (sp. gr. 1.13), and expel the nitrous fumes by boiling. Add about 0.5 grm. of sodium bismuthate, a little at a time to the boiling solution, to destroy any carbonaceous material. If a brown precipitate of manganese forms, add 2 or 3 drops of concentrated sulphurous acid to clear it, cool, and add a large excess of bismuthate (2 grm.). Allow the mixture to stand for five minutes and then filter it through clean asbestos. Wash the residues with 100 ml. of 3 per cent. nitric acid (30 ml. of concentrated acid diluted to 1 litre). Add 50 ml. of 2 : 1  $H_2SO_4$  and cool to at least 30° C. Titrate with a solution of mercurous nitrate made as follows: Dissolve 10 grm. of the salt in 150 ml. of water acidified with 2 ml. of nitric acid. After allowing to stand for some hours, filter, and dilute to 1 litre.



Standardise the mercurous nitrate solution against permanganate by placing a known volume of the standard 0.05 N. permanganate in the titration vessel, with 50 ml. of 2 : 1  $H_2SO_4$  and 200 ml. of water. In order to make the conditions of the assay and the standardisation alike, add also 25 ml. of concentrated  $HNO_3$ . Any nitrous acid which may have been present in the nitric acid should have been removed by shaking it with sodium bismuthate and the excess of sodium bismuthate should, in its turn, have been completely removed by filtration.

**Determination of Chromium in Steel.** Dissolve 2 grm. of the steel in 100 ml. of dilute sulphuric acid (1 : 3), and, in order to decompose carbides, evaporate until salts begin to separate. Dilute to 50 ml. Add 3 ml. of concentrated nitric acid and boil, to oxidise the iron and to expel nitrous fumes. Dilute further to 300 ml., and oxidise the chromium to dichromate by adding to the boiling solution 1 grm. of silver nitrate followed by a concentrated, aqueous solution of ammonium persulphate containing 10 grm. of the salt. Boil for ten minutes, and then add 5 ml. of 1 : 3 HCl to decompose any permanganic acid which will be present if the steel contained manganese. (Some prefer to add manganese sulphate as an indicator, as the production of a pink colour shows that the oxidation of the chromate is probably complete.) After the addition of the HCl, boil for five minutes to remove any chlorine which may now be present. Cool, and titrate with a standard solution of ferrous sulphate; a 0.05 N. solution is often suitable.

The chromium in ferro-chromium may be determined by decomposing the alloy with sodium peroxide (p. 258). The hot solution should be treated with persulphate exactly as is described above, but 100 ml. of dilute sulphuric acid (1 : 3) should be present in the liquid during the titration.

**Determination of Vanadium in Steel.** The method is based on the fact that pentavalent vanadium can be reduced quantitatively to the quadrivalent state by ferrous sulphate. The vanadium is first oxidised to the pentavalent state by silver persulphate.

Take 1 grm. of the steel, or, if the sample contains less than 0.5 per cent., 2 grm. Dissolve in 40 ml. of 1 :  $\text{H}_2\text{SO}_4$  and 40 ml. of water. Add 3 ml. of concentrated  $\text{HNO}_3$  to dissolve carbides and to oxidise the iron. Boil off the nitrous fumes. Dilute to 300 ml. with hot water and oxidise the vanadium quantitatively, as described for chromium (p. 217). Cool, to at least  $10^\circ \text{C}$ . Titrate with 0.05 N. ferrous sulphate. At first there is a gradual fall in the potential of the cell, which becomes even slower as the titration proceeds. The end-point is marked by a sudden, rapid decrease. If the titration is over-shot, back-titrate with 0.05 N. potassium dichromate.

If the curve obtained is not sharp, it can be improved by changing the concentration of the sulphuric acid or by diluting the solution, or by both modifications. The concentration of acid tends to become too low, and the concentration of vanadium too high.

This method can be carried out in the presence of tungsten, if that element is not present in great excess. In the presence of chromium do not oxidise the vanadium with persulphate because the chromium is also attacked. Dissolve the sample as before. After the first addition of  $\text{HNO}_3$ , dilute to 200 ml. and add a further 40 ml. of concentrated  $\text{HNO}_3$ . Oxidise the vanadium by boiling this solution for at least one hour; at least half the liquid must be removed by evaporation. Cool, dilute to 300 ml. and titrate as before. Nitric acid is a poor oxidising agent, and as the vanadium is never completely oxidised by it, it is usual to add 1 per cent. to the result obtained.

For an alternative method for determination of vanadium in the presence of chromium, see under Ferro-Vanadium below.

**Determination of Vanadium and Chromium in Ferro-Vanadium.** Dissolve 3 grm. of the sample in 50 ml. of nitric acid (sp. gr. 1.2). When solution is almost complete, add 10 ml. of  $\text{HCl}$  to complete the decomposition of such carbides as are present. Reduce the volume to one-half by evaporation, and add a few drops of hydrofluoric acid to remove silica. Evaporate with 50 ml. of concentrated  $\text{H}_2\text{SO}_4$  until dense fuming occurs, to remove the  $\text{HCl}$ . Cool. Dilute, and make up to 1 litre. Any solid residue should be tested for vanadium and chromium; if those elements are found, the residue should be fused with sodium peroxide and the sodium vanadate and chromate extracted with hot water. The resulting solution should be acidified with dilute sulphuric acid and added to the contents of the flask.

Oxidise a portion of the solution with silver persulphate and titrate it electrometrically with ferrous sulphate (p. 217). The titration gives a value for the chromium and the vanadium, the dichromate being reduced to  $\text{Cr}^{+++}$  and the  $\text{V}^{++++}$  to  $\text{V}^{+++}$ . It will be necessary to add the ferrous sulphate in slight excess in order to find the end-point. Add enough ferrous sulphate to increase this excess to about 5 ml., and titrate in the cold with a solution of ceric sulphate. This will oxidise the iron to the ferric state and leave tetravalent vanadium. Add enough sulphuric acid

to bring the concentration of this acid to 15 to 20 per cent. by volume, heat to 80° C., and continue the titration with ceric sulphate. Pentavalent vanadium will now be formed, but the chromium will not be oxidised. Standardise the solution of ceric sulphate against a standard solution of ferrous ammonium sulphate.

**Determination of Uranium.** This method depends on the fact that the uranium in a solution can be reduced to the trivalent condition by zinc and sulphuric acid. On subsequent treatment with permanganate or ceric sulphate the uranium first becomes tetravalent and finally hexavalent. The completion of these two stages is shown by well-marked breaks on the titration curves.

Make up a solution of uranium sulphate or chloride (or acetate, if the Jones reductor is not to be used), containing about 0.01 gm. of uranium per millilitre. Nitrate must be absent. Either reduce 25 ml. of the solution in a Jones reductor, or place 25 ml. in a conical flask, add a considerable excess of dilute sulphuric acid, and reduce with granulated zinc at 60° C. This reduction must be continued for at least half an hour, and all the zinc must be dissolved. Dilute to about 200 ml. with air-free water, and titrate with decinormal potassium permanganate or decinormal ceric sulphate.

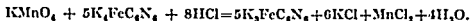
If the Jones reductor is used, the uranium will probably be reduced to some indeterminate state between the trivalent and tetravalent conditions. This is of no consequence, because the definite steps in the titration curve mark the change from  $U^{4+}$  to  $U^{6+}$  exactly. The uranium may also be reduced past the tetravalent state if granulated zinc is used, though there then is some risk that complete reduction to this state may not have been effected.

If iron is present it is, of course, reduced in the reductor, but it is not again oxidised until all the uranium is in the hexavalent state. The completion of the oxidation of the iron is marked by a third, sudden increase in the potential.

**Determination of Zinc** electrometrically, by direct titration with potassium ferrocyanide according to the equation



The method is unsatisfactory because the reaction is so slow near the equivalence point that the potential takes a long time to become constant. Even if the solution is heated to 65° C., one titration takes at least half an hour. Moreover, the titration curve is flattened out if the acid concentration is at all high. An accurate determination can however, be made rapidly by precipitating the zinc with an excess of potassium ferrocyanide and by back-titrating this excess with potassium permanganate.



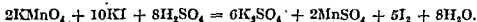
To standardise the potassium ferrocyanide, dissolve 1.5 gm. of zinc in the least possible quantity of hydrochloric acid, and dilute the solution 500 ml. Take 10 ml. of this solution and dilute it with 25 ml. of dilute  $H_2SO_4$  and 50 ml. of water. Add a large excess (50 ml.) of potassium ferrocyanide solution (about 20 gm. of  $K_4FeC_6N_6 \cdot 3H_2O$  per litre) slowly,



with constant stirring. Titrate this excess with decinormal potassium permanganate or ceric sulphate. The end-point should be quite sharp. Any metal which gives an insoluble ferrocyanide interferes with the reaction and should be removed. Similarly, find the volume of permanganate or ceric sulphate required to react with 25 ml. of the ferrocyanide.

The determination of zinc should be carried out under conditions which resemble as closely as possible those under which the ferrocyanide was standardised.

**Determination of Hydriodic Acid with Permanganate.** This method is based on the reaction :



If chlorides and bromides, especially the latter, are present, they may also be attacked by the permanganate, and the results of ordinary volumetric analysis are unreliable. The electrometric method, on the other hand, gives a good result, provided that the quantity of chlorine present is not more than the equivalent of the iodine and the quantity of bromine not more than one-quarter of that equivalent.

The iodide solution and the permanganate solutions should be about 0.05 N. Place 20 ml. of the iodide solution in the titration vessel, and dilute to 200 ml. with water and sulphuric acid in such a way that the final acid concentration is nearly normal. Stir vigorously by blowing washed air through the liquid, and titrate with the permanganate. The end-point is marked by an abrupt rise in voltage.

The iodide and bromide can be determined in one titration when they are present together, and if the conditions are chosen correctly, the oxidation of each halide is marked by a break in the titration curve.

*Note.* Only a few examples of the very numerous electrometric titrations have been given here. For further information and a long list of methods, consult the 12th Edition of *Sutton's Volumetric Analysis*. See also *Potentiometric Titrations*, by Kolthoff and Furman.

## CONDUCTOMETRIC ANALYSIS

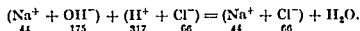
**Principle of the Method.** Measurements of the conductivities of solutions have been carried out for the purposes of theoretical physical chemistry for many years, but it is only comparatively recently, owing to certain simplifications in the method, that these have attained importance in chemical analysis. The principle of the method is the measurement of the change in the electrical resistance of a solution while it is being titrated, just as in potentiometric methods the change in potential is measured. It is found that under certain conditions this resistance undergoes a change at the end-point, which enables the latter to be indicated.

The electrical resistance of an aqueous solution depends primarily on the nature and concentration of the ions present, and in particular on their velocities of travel through the solution, since this determines largely the readiness with which electrical charges are passed on from one ion to another. The table shows the mobility of some common ions at 18° C.

Anions	Mobilities	Cations	Mobilities
$\text{H}^+$	317	$\text{OH}^-$	175
$\text{K}^+$	64	$\text{Br}^-$	68
$\frac{1}{2}\text{Ba}^{++}$	55	$\frac{1}{2}\text{SO}_4^{--}$	68
$\text{Ag}^+$	54	$\text{I}^-$	66
$\frac{1}{2}\text{Zn}^{++}$	46	$\text{Cl}_3^-$	66
$\frac{1}{2}\text{Cu}^{++}$	46	$\text{NO}_3^-$	62
$\text{Na}^+$	44	$\text{CH}_3\text{COO}^-$	35
$\text{Li}^+$	33	$\text{IO}_3^-$	34

It will be seen that the values for the  $\text{H}^+$  and  $\text{OH}^-$  ions (derived from an acid and alkali, respectively) are much greater than those of any of the other ions; solutions containing such ions therefore, will have a relatively low electrical resistance. For the present purposes it is usual to refer not to resistance but to conductivity, the reciprocal of resistance. Therefore, the lower the resistance the higher the conductivity.

Now consider the simple neutralisation of 0.1 N.  $\text{HCl}$  by 0.1 N.  $\text{NaOH}$ . Expressed ionically the equation is



The mobilities in round numbers, are shown underneath the respective ions. The water formed in the reaction supplies no ions to conduct a current. Suppose that the acid is in the titrating vessel. It will have a high conductivity because of the combined effects of the mobilities of the  $\text{Cl}^-$  and (particularly) of the  $\text{H}^+$  ions (see table). On adding the alkali, the  $\text{OH}^-$  it provides will take up the  $\text{H}^+$  ions of the acid, producing  $\text{H}_2\text{O}$  and thereby eliminating both  $\text{H}^+$  and  $\text{OH}^-$  ions so far as their capacity to conduct electricity is concerned. At the end-point, the removal of  $\text{H}^+$  ions will be complete, and the conductivity will have fallen correspondingly, because the mobilities of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions also present will be far from sufficient to compensate for this. The first drop of  $\text{NaOH}$  added after the end-point can now supply  $\text{OH}^-$  ions which have no  $\text{H}^+$  to neutralise them, and as their mobility is high, the conductivity will rise sharply and will continue to do so while  $\text{NaOH}$  is being added. If therefore, the conductivity is plotted against the number of ml. added, a curve such as XYZ in Fig. 92 (p. 223) will result, from which the end-point is readily obtainable.

This simple reaction has been chosen as an example, but similar arguments apply to other and more complicated reactions. The method is also being used increasingly in industry for the continuous control of the compositions of flowing liquids (e.g., water-supplies), since any change in the ionic composition of these will result in a change in conductivity. Automatic recording instruments have been developed for such purposes, but these applications are outside of our present scope (see reference, p. 518).

**Apparatus Required.** In its simplest form the apparatus comes well within the facilities of an ordinary laboratory, and it is shown in diagram in Fig. 90. This is really an adaptation of the ordinary Wheatstone

bridge method of measuring electrical resistance, the arms of which are a standard resistance ( $R$ ), the titration vessel ( $V$ , see also Fig. 91) whose resistance or conductivity is to be measured, and the two portions of the

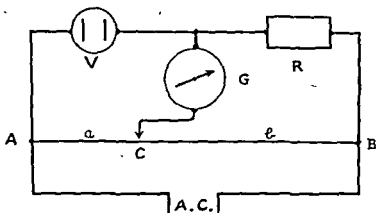


FIG. 90. CONDUCTIVITY CIRCUIT.

potentiometer measuring wire ( $AB$ ), the relative lengths of which ( $a$  and  $b$ ) are varied by means of the sliding contact ( $C$ ). The apparatus is to some degree analogous to that used for potentiometric measurements (p. 210).

The principal points of difference are the source of current, which must be about 2 volts A.C. (see below), and the null-point instrument, which correspondingly must be sensitive to alternating current. The former may be obtained from a high voltage A.C. supply by means of a suitable transformer; an induction coil may also be used, but is rather noisy unless it is placed at a distance or suitably screened. The null-point instrument ( $G$ ) may be an A.C. galvanometer, or a thermionic valve rectifier; the latter has the advantages of convenience and efficiency at relatively little cost, and simple circuits are to be found in the book cited on p. 518.



FIG. 91.  
CONDUCTIVITY  
CELL.

A convenient titration vessel (Crocker and Matthews) is shown in Fig. 91. It consists essentially of two platinised platinum electrodes (p. 211), held vertically and at a distance apart which should be adjusted according to the conductivity of the solution to be titrated. Provision is made for the insertion of the tip of a burette into the vessel, for a stirrer, and for temperature control (e.g., by immersing the vessel in a thermostat). A mercury contact (p. 211) may be used to connect the electrodes with the rest of the circuit, and this is done irrespective of their polarities, as A.C. is involved. Direct current cannot be used because it would tend to electrolyse the solution, and the minute gas bubbles of hydrogen and oxygen thus formed at the cathode and anode, respectively, would raise the electrical resistance of the system and introduce a disturbing factor. These bubbles do not form if A.C. is used.

Titration should be carried out with a micro-burette (p. 114), and the

solution being added should have a concentration about 10 times that present in the titrating vessel; the use of a micro-burette which can be read to 0.01 ml. counteracts any error due to titration with such a concentrated solution. The object of this difference in concentrations is to avoid any marked increase in the volume of the contents of the titration-vessel owing to the addition of the titrating solution, because as already pointed out, the mobilities of the ions vary according to their concentrations.

**Procedure.** For practice, titrate 20 ml. of 0.1 N. HCl with 0.1 N. NaOH. Carefully clean the titration-vessel, and rinse it well with distilled water. Place the 20 ml. of 0.1 N. HCl in it, and connect up as shown in Fig. 90; switch on the current. Adjust the standard resistance so that the null-

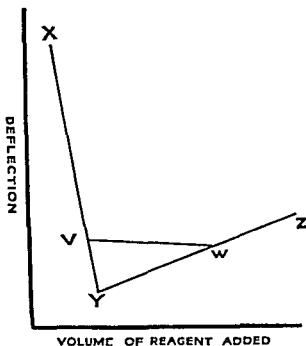


FIG. 92. CONDUCTIVITY CURVES.

point instrument registers the passage of no current (or of a minimum of current) when the sliding contact is approximately in the centre of the potentiometer slide-wire. If ear-phones are used, this point is indicated by the minimum of sound being heard; a noisy induction coil may then be found disadvantageous. Start the stirrer, allow the temperature to become constant and ensure that it does not alter by more than  $\pm 1^\circ \text{C}$ . during the titration; the conductivity is very susceptible to temperature changes.

When the reading of the slide-wire is constant, note it, and start to add the NaOH from the micro-burette, in 0.2-ml. portions. Adjust the sliding contact after each addition so as to obtain a null-current indication, and note the reading when it has become constant. Continue titrating in this way, but, as the end-point is approached, add 0.1-ml. portions and then the minimum amount that can be delivered from the burette.

If the apparatus is connected as shown in Fig. 90 the sliding-contact

will have to be moved gradually to the right as titration proceeds. After the end-point however, when the conductivity is a minimum, it will be necessary to start to move it to the left, and it is advisable to carry the titration well beyond this point, so as to obtain a complete curve of the type XYZ shown in Fig. 92. Plot the results obtained in this way, and if the point of the curve is not very sharp at the end-point, extend the two straight inclined arms downwards until they meet at an angle, and take this as the end-point. Compare the result with that obtained by direct titration by the iodate method (p. 180).

*Note.* If a valve rectifier end-point indicator is used, manipulation of the sliding-contact is unnecessary as an ordinary galvanometer is suitable. Once the instrument is set, therefore, it is necessary only to note the galvanometer deflection after each addition of reagent. This method, therefore, is greatly to be preferred for rapid routine analytical work.

It will be seen that the method enables results to be obtained independently of many influences which affect the accuracy of ordinary indicators, such as colour or turbidity in the original solution. The method is also preferable to potentiometry in certain cases where the latter method is affected by electrode poisons which may be present in the solution in small quantities. It will be appreciated too, that where a "curve" of the type XYZ shown in Fig. 92 is obtained, the result may be deduced very rapidly, because it is necessary only to establish 2 or 3 points on each of the straight line arms to be able to draw these arms, and so obtain their point of intersection. On the other hand, the special precautions indicated (e.g., as regards temperature, concentration, etc.) must be observed strictly.

Examples of Applications of a less simple nature, some of which are carried out more conveniently by conductometric than by other methods, are given below.

**Salts of Weak Acids or Bases.** Titrate a 0.01 N. sodium acetate solution with 0.1 N. HCl. At first there is little change in the conductivity, because the free acetic acid liberated contributes little to the conductivity, and the replacement of the acetate by chloride ion has little influence on it (cf. Table). At the end-point, however, the excess of free  $\text{H}^+$  and  $\text{Cl}^-$  ions causes a rapid increase in conductivity, and a curve of the type shown by VWZ in Fig. 92 results. If the junction of the two lines is rounded, the true end-point may be found by extending the straight portions of the two arms until they meet.

**Precipitation Reactions.** Titrate 0.01 N.  $\text{AgNO}_3$  with 0.1 N. NaCl, as already described. As titration proceeds AgCl will be precipitated, and the effects of the mobilities of the  $\text{Ag}^+$  and  $\text{Cl}^-$  ions will be eliminated; at the end-point, the first excess of NaCl will contribute  $\text{Na}^+$  and  $\text{Cl}^-$  ions, and therefore, a curve of the type XYZ shown in Fig. 92 will result, although the actual end-point may not be well-defined, because the high mobilities of the  $\text{H}^+$  and  $\text{OH}^-$  ions will not be involved. A study of the table suggests that LiCl is to be preferred to NaCl by reason of the steeper slope it produces on the left arm of the curve; this is indeed found to be the case, but this reagent is relatively expensive.

Other applications are to the titration of zinc as ferrocyanide (p. 199); of sulphates with barium chloride (p. 174); and of mixtures of strong and weak acids.

## ELECTRODEPOSITION ANALYSIS

The subject of electrode potentials has already been discussed (p. 205). When a bar of zinc is placed in a solution of one of its salts, the concentration of the ions in the solution being molar, the potential between the metal and the solution, with reference to the normal hydrogen electrode, is  $-0.76$  volt. As zinc has a marked tendency to ionise, the bar is left with a negative charge; similarly the half-cell potential between copper and copper sulphate solution is  $+0.33$  volt.

The following table gives the principal standard electrode potentials:

Metal	Potential (volts)	Metal	Potential (volts).
Na	$-2.64$	Co	$-0.27$
Mg	$-1.55$	Ni	$-0.24$
Mn	$-1.08$	Sn	$-0.14$
Zn	$-0.76$	H	$0.00$
Fe	$-0.43$	Cu (divalent)	$+0.34$
Cd	$-0.40$	Ag	$+0.79$

The potential which must be applied across two platinum electrodes placed in a normal solution of zinc sulphate in order to decompose the salt is  $2.35$  volts. The Table shows that there is a difference of  $(-0.76 - 0.33) = -1.09$  volt between the standard electrode potentials of zinc and copper, and, as the salts of the more electro-negative metals are the easier to decompose, it follows that a potential difference of  $(2.35 - 1.09) = 1.26$  volt would be required to decompose a normal solution of copper sulphate, while the decomposition potential of silver sulphate would be about  $0.82$  volt (subsidiary effects are being neglected). Thus, if a solution containing silver sulphate and copper sulphate is electrolysed with a potential difference of  $1$  volt, only silver would be deposited on the cathode. The principle of "graded electrolysis" should now be evident.

It has been pointed out on p. 206 that the electrode potential is not a constant, but depends on the concentration of the ions in the solution; and that for a monovalent metal, such as silver, the equation becomes

$$E = 0.058 \log_{10} \frac{p}{P},$$

where  $p$  is the osmotic pressure of the ions and  $P$  is a constant.

It follows that if  $0.82$  volt is required to decompose a molar solution of silver sulphate,  $(0.82 + 0.058 \log_{10} 10) = 0.878$  volt will be required for a decimolar solution,  $0.936$  volt for a centimolar solution, and so on. Thus, in the case mentioned above, electrolysis will stop when the concentration of silver ion in solution is reduced to about millimolar, so that, although a completely quantitative separation of two metals by electrolysis is theoretically impossible, a separation good enough for practical purposes can be achieved, provided the electrode potentials of the two metals involved are sufficiently dissimilar.

It follows, from what has been said already, that, if a molar solution of copper or silver, to which dilute acid has been added, is electrolysed, practically all the copper or silver can be deposited before any hydrogen

will be evolved from the cathode. But if an attempt is made to deposit an electro-negative metal such as zinc from a solution, molar both with respect to the zinc and to hydrogen ion, the current will spend itself in the production of hydrogen gas and no metallic zinc whatever will be obtained.

The  $P_H$  of the solution will have to be increased to  $\frac{0.76}{0.038} = 18$  before any zinc will be deposited, although, in practice, this metal can be obtained from less alkaline solutions. Similarly, as the  $P_H$  of solutions from which metallic sodium could be obtained would theoretically be about 47, sodium cannot be deposited in the presence of water. Thus, the intermediate electro-negative elements can be deposited only from weakly acidic or alkaline solutions.

Furthermore since metallic ions usually diffuse extremely slowly, the solution immediately near the cathode may be denuded of the metallic ion; therefore, although the average concentration of the solution would seem to make hydrogen discharge unlikely, the local concentration may make it possible. If metal and hydrogen ions are being deposited simultaneously, the deposit is likely to be non-adherent and porous. A porous deposit will probably contain entrapped mother-liquor. To overcome this effect it is either necessary to use a low current density, in which case the electrolysis will take a long time, or to increase the speed of migration of the ions by heating the solution, or by violent stirring.

### Apparatus

The simplest form of apparatus is shown in Figs. 93, 94 and 95. It consists of an anode (Fig. 93) and a cathode (Fig. 94), usually of platinum,

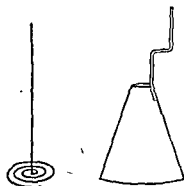


FIG. 93.  
ANODE.

FIG. 94.  
CATHODE.

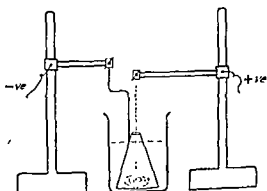


FIG. 95. ARRANGEMENT OF STATIONARY ELECTRODES.

although, for certain specific analyses, other metals can be employed. These electrodes and the electrolyte are arranged as shown in Fig. 95. When it is necessary to carry through a large number of similar determinations, the anodes and cathodes can be held by two bars in such a way that a large number of the cells are in parallel with each other.

The chief objection to this form of apparatus is that the electrolyte is not stirred, and therefore the current density must be low, and, in consequence, the deposition of the metal may take hours. For example, with Sand's rotating electrodes (described below) it is possible in twenty

minutes to deposit quantitatively a weight of copper which would require some ten hours by the simpler apparatus. Even after the expiration of ten hours some of the copper would probably be left in the solution, and for exact work a supplementary colorimetric determination of this residue would be required.

**Rotating Electrode.** An apparatus suitable for the rapid determination of many of the metals is shown in Figs. 96 to 99. The cathode (Fig. 96) and anode (Fig. 97) are made of platinum gauze. Suitable dimensions for the

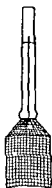


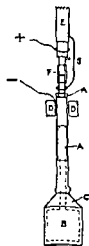
FIG. 96. GAUZE CATHODE.



FIG. 97. GAUZE ANODE.

cylindrical part of the electrodes are 4 and 3.0 cm. in height and 3.5 and 2.5 cm. in diameter, respectively. The gauze should not be too fine, fourteen strands of 34 S.W.G. wire to the linear centimetre being a suitable size, and small recesses or roughnesses on the surface of the cathode should be avoided as far as possible, because these are apt to contain electrolyte which is trapped by the spreading film of deposited metal.

The method of fitting the electrodes together is shown in Fig. 98. The electrodes are insulated from each other by a glass sleeve, A. The top of this sleeve should be smooth, but slightly belled out so that it is impossible for the tube to slip down the stem of the anode. The bottom of the sleeve should also be smooth, but neither larger nor smaller than the average diameter of the tube. It is most important that this tube should be the correct size. The anode, B, should just be able to turn easily in it, while the cathode, C, should fit it tightly. If the internal diameter is too large, the electrodes are apt to wobble when the anode is running at a high speed. This may cause loss in weight of the anode through abrasion; at best, it causes unnecessary noise. The cathode is held tightly, but not too tightly, in a stand whose jaws, DD, are covered with thin platinum foil so that an electrical connection can easily be made. The anode is attached, by means of a close-fitting rubber tube, F, to a brass rod, E, which can be rotated. Electrical connection is made here by a platinum spring, G. The circuit is outlined in Fig. 99. The brass rod, S, to which the anode is fitted, carries a pulley wheel, P, which can be rotated by an electric motor. A battery of eight accumu-

FIG. 98.  
ARRANGEMENT  
OF SAND'S  
ELECTRODES



lators so arranged that current can be taken from as many of the cells as is desired, is a convenient source of current for the electrolysis. The positive terminal is connected through an ammeter, *A*, to the anode. The negative terminal is connected to the cathode thorough a small variable resistance, *R*, and a key, *K*. A voltmeter, *V*, is connected across the anode and cathode as shown.

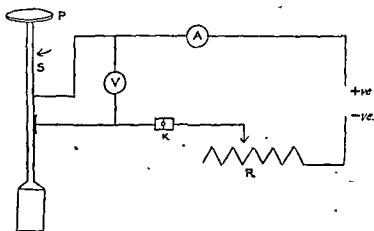


FIG. 99. GENERAL ARRANGEMENT OF ELECTRODEPOSITION APPARATUS WITH ROTATING ANODE.

Narrow beakers ensuring the smallest practicable volume of liquid between the cathode and the glass, are most suitable for use as electrolytic vessels. The apparatus should be so arranged that the beaker can be removed easily without touching any part of the apparatus, and so that the electrolyte can be warmed when necessary.

### Determination of Copper

**Stationary Electrodes.** For practice, weigh out about 0.3 gram. of copper into a 150-ml. beaker. Cover with a watch-glass and dissolve the copper in the least possible volume of 50 per cent. nitric acid. Heat gently if necessary. When solution is complete, partially remove the cover and boil off nitrous fumes. Cool. Wash down the watch-glass and the sides of the beaker. Neutralise with ammonia. Add 3 ml. of sulphuric acid and 2 ml. of 4 : 1 nitric acid (which has been boiled to expel any oxides of nitrogen), and dilute to 100 ml. Electrolyse with a current of about 0.5 amp. and a potential difference of about 2 volts. The beaker should be covered with a split watch-glass to prevent loss by spraying. Deposition will be practically complete after eight hours. Either continue until it is complete, or break off the experiment and determine the residual copper colorimetrically.

The cathode may be prepared for weighing as follows: Rinse it thrice with distilled water, once with methylated spirits, and dry it in a steam-oven. Allow it to cool in a desiccator for a short time (three to five minutes) before weighing it. For results of the highest accuracy, prepare and weigh the cathode before and after the deposition of the copper in exactly the same way.

If the deposit is bright and clean, the cathode can be used at once for a second determination. If desired, the copper can be removed from a

platinum electrode by dipping in hot, 50 per cent. nitric acid. If the deposit is small, it is a good plan to do this and to determine the copper in the solution colorimetrically (p. 238) as a check.

The time required for the analysis can be reduced to about two hours by maintaining the electrolyte at 70° to 80° C., but, unless the conditions are correct, the copper may be precipitated in a spongy form or it may be oxidised. The solution must be absolutely free from chlorine, which causes the copper to deposit in spongy form, and also partial solution of the anode and deposition of the platinum on the cathode.

*Note.* Test qualitatively for copper in the electrolyte by the diethyldithiocarbamate method (p. 239) as follows: Withdraw 2 drops of the solution and place them on a white tile. Add 1 drop of a solution containing 200 grm. of citric acid per litre, to prevent interference by iron, if present. Make alkaline with a drop or two of 0.880 ammonia, to prevent interference by zinc, if present, and add 1 drop of a 0.1 per cent. solution of the reagent. A dark brown colour denotes the presence of copper.

This test has : . . . . . so sensitive. It can detect 0.001 milligram . . . . . In this particular case, the electrolysis can . . . . . milligram of copper is left in solution, and this quantity will give a marked reaction. It is therefore advisable to have a solution containing 0.1 milligram of copper per 100 ml. at hand, and to compare the reaction obtained from 2 drops of this standard with that from 2 drops of the electrolyte.

In the absence of interfering elements, the ferrocyanide test (p. 239) is to be preferred.

*Rotating Electrode in Sulphuric Acid.* Clean the cathode, dip it in methylated spirits, and dry, cool, and weigh it under standard conditions. Revolve the anode by hand, and make sure that it is running freely without abrasion. Connect up the current and again rotate the anode. If the needle of the ammeter flicks, there is a contact somewhere between the anode and cathode. Start the motor, see that it is not running too fast, and that all is in order. Stop the motor.

Meanwhile the copper should have been dissolved in the least possible quantity of 50 per cent. nitric acid, using the beaker to be used in the electrolysis. Rinse in the cover and wash down the beaker, using the least possible quantity of water. Add 6 to 7 ml. of dilute sulphuric acid, sufficient to convert the copper nitrate to sulphate, and evaporate until dense white fumes are evolved, to expel the nitric acid. Cool. Dilute to 50 ml. with water, and neutralise with ammonia. Add 20 ml. of normal sulphuric acid and bring the volume of the solution to 100 ml.

Arrange the electrodes in the solution and cover the beaker with a split watch-glass. At the beginning of the experiment, all the external resistance should be in the circuit, so that only a small current will be passing. Start the motor, and raise the current to 0.5 amp.; three lead accumulators should be sufficient. When the platinum has been covered by a visible film of copper, reduce the external resistance until the current is about 2 amps., when the potential difference between the electrodes will be about 2.5 volts, and heat the contents of the beaker to about 70° C.

After some fifteen minutes the solution will be practically colourless. At this stage, wash in the spray from the watch-glass and from the sides of the beaker. Test the solution with diethyldithiocarbamate or ferrocyanide (see *Note* above). Leave the current on and the motor running, and remove the electrolyte by means of a reversed 100-ml. pipette (so that

the liquid enters through the wide end), and at the same time add distilled water, keeping both electrodes always covered. When all the electrolyte has been replaced by distilled water, there is no risk that the deposit will redissolve, and the ammeter should now indicate less than 0.1 amp. Remove the second beaker. Cut off the current. Stop the motor. Remove

the cathode, dip it in spirit, dry and weigh it.

*Rotating Electrode in Nitric Acid.* Take 0.5 gm. of copper, or that quantity of a copper alloy which is thought to contain 0.5 gm. of copper, and dissolve the metal in 10 ml. of concentrated nitric acid, using the same covered beaker in which it is to be electrolysed. Boil off the nitrous fumes. Cool. Add ammonia until the blue colour of the complex ion is just developed, or until a precipitate just forms. Add sufficient nitric acid to give a concentration of 9 ml. of the concentrated acid per 100 ml. of the final electrolyte. Dilute, and add a few crystals of urea to remove completely any traces of nitrous acid. Cool, to at least 20° C. Electrolyse as before, starting with a low current and increasing to 1.5 amp. after a short time. As soon as the solution is colourless, wash in the spray and add about 0.5 gm. of urea. Continue the electrolysis for three minutes. Test, wash, disconnect, and dry as before.

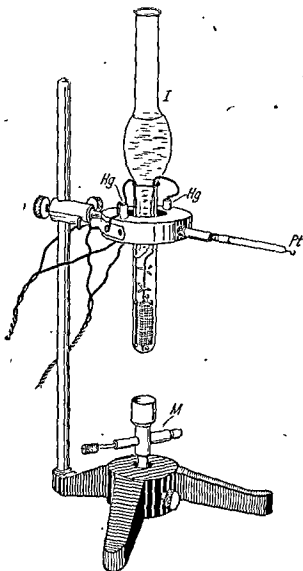


FIG. 100. APPARATUS FOR THE MICRO-ELECTRODEPOSITION OF COPPER. (One-third actual size.)

*I*, Condenser. *Hg*, Mercury contacts. *Pt*, Platinum hook. *M*, Micro-burner.

this excess produces a considerable quantity of ammonium nitrate in the solution. This is desirable, because copper is more easily precipitated in a bright and coherent form in the presence of this salt. Care should be taken, when removing the nitrous fumes, to avoid the loss of much nitric acid.

The Micro-Electrodeposition of Copper is very easily carried out by the apparatus shown in Fig. 100; a sensitivity of 0.005 milligram is obtainable. The electrolysis vessel is the cut-off base of a boiling tube,

in the top of which is supported a test-tube (I), containing water, to serve as a condenser. The cathode is the platinum gauze cylinder, 10 mm. in diameter and 30 mm. long, and it encircles the platinum wire anode as shown, without touching it. The terminals are connected in series with two accumulators and a sliding resistance; and independently, to the terminals of a voltmeter in parallel.

Wash the cathode in nitric acid, and rinse, ignite and weigh it. Place the solution to be analysed (containing about 1 milligram of Cu) in the lower tube so as just to cover the cathode, add 1 drop of dilute sulphuric acid, bring just to the boil by means of the micro-burner (M), and connect up the circuit as described. During electrolysis keep the solution boiling gently, and adjust the resistance so that the voltage is always 2. After about fifteen minutes, lift out the two electrodes together, and rapidly wash the cathode. Then dip it successively in alcohol and in ether, dry it high above a Bunsen flame (so that the ether does not ignite), and reweigh it. If the weight is small, check it by dissolving off the deposit in acid and matching it colorimetrically (p. 238).

### Determination of Nickel and Cobalt

Nickel, an electro-negative element, is usually deposited from a strongly ammoniacal solution of the sulphate, though ammoniacal solutions of the nitrate or the chloride may be used, provided certain precautions are taken. The determination may be carried out rapidly with the rotating electrode.

For practice, weigh out about 2 grm. of nickel ammonium sulphate,  $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , directly into a suitable beaker, and dissolve the salt in a little water. In order to increase the conductivity, add 3 grm. of ammonium sulphate for every 100 ml. of final electrolyte, which should also contain 25 ml. of concentrated ammonia (sp. gr. 0.880). Warm to  $50^\circ \text{C}$ ., and electrolyse, using a current of about 1.5 amp. at a potential difference of 2.5 to 3 volts. Four accumulators will probably be required. Deposition should be complete in about half an hour. Wash in the spray, and test for nickel by adding a drop of the solution to a drop of freshly-made ammonium sulphide solution on a white tile. If there is at first no brown stain of nickel sulphide, reduce the alkalinity of the liquid on the tile, because nickel sulphide is somewhat soluble in a strongly ammoniacal solution of ammonium sulphide.

The deposit of nickel on the gauze cathode should be bright and shining. It is washed, without breaking the current, cleaned and dried, in exactly the same way as in the determination of copper (see above). The gauze may be used again without treatment, or the nickel may be dissolved in boiling nitric acid.

At the start of the deposition, a dark-brown deposit may appear. This may dissolve and cause no trouble. Its continued presence is a sign either that the solution does not contain enough ammonia or ammonium sulphate, or that the current-density is too high. The current-density should be low, until a shining film of the metal has been provided; it may then be increased.

Cobalt can be determined in exactly the same way as nickel. As it is more easily oxidised than nickel, the results may be high. They may also be low, as sometimes cobalt dioxide is deposited on the anode. It is advisable, therefore,

to reduce the current to about one-half of that required for nickel and to reduce the potential difference correspondingly.

On electrolysis, an ammoniacal solution containing copper, nickel and cobalt, deposits these three metals quantitatively on the cathode. It is usual to remove

### Determination of Cadmium

Although cadmium can be deposited from a solution of the metal in dilute sulphuric acid, quantitative results are easier to obtain by using an alkaline cyanide solution.

Dissolve about 0.4 gm. of cadmium (as the sulphate) in a little water. Add 1 drop of phenolphthalein, and run in dilute sodium hydroxide until a permanent red colour has been obtained. Add a 10 per cent. solution of potassium cyanide until the precipitate has completely dissolved. The liquid must be stirred when this addition is being made, and a large excess of the cyanide must be avoided. Dilute to 100 ml. Heat to 60° C., and electrolyse with a current of 0.1 amp. which may shortly be increased to 0.5 amp. The metal should deposit as a silvery-white film. Provided the platinum cathode is not heated above 100° C. when it is dried, there is no need to protect the platinum with a coating of copper, as with zinc (see below).

The solution may be tested for cadmium by withdrawing some drops of it with a pipette, removing the cyanide by heating the liquid in a clean white dish with a little dilute hydrochloric acid, and by adding a few drops of saturated  $H_2S$ -water. The absence of a yellow coloration may indicate that precipitation is complete. This coloration will not appear, even if cadmium is present, if there is too much hydrochloric acid in the dish.

The cyanide must not be removed in the open laboratory.

### Determination of Zinc

Zinc can be deposited from alkaline, ammoniacal, or weakly acid solutions. Zinc easily alloys with and covers the cathode to cover it. This is done by using

the electrolytic method, but the method is included here as it is an instructive exercise. For practical purposes, the determination of zinc volumetrically as ferrocyanide or gravimetrically as oxide is to be preferred.

**Alkaline Solution.** Take about 0.3 gm. of zinc, or the corresponding weight of zinc sulphate. Dissolve the zinc in the least quantity of dilute sulphuric acid, neutralise with sodium hydroxide and add enough in excess to make the concentration of alkali 4N. The solution should be quite clear. Heat to 70° C. and electrolyse, using a current of about 0.5 amp. at 3 volts. Deposition should be complete in three-quarters of an hour. The solution should be cooled to room temperature before the electrolyte is removed. If nitrates or ammonium salts are present, it is difficult to obtain quantitative precipitation of the zinc.

**Acetic Acid Solution.** Prepare a solution of zinc in dilute sulphuric acid, or of zinc sulphate in water, such that the solution contains about 0.1 gm. of zinc. Can be used for 10 dts. As is precipitated quantitatively only at temperatures below 30° C., it may be necessary to stand the beaker in a vessel of cold water. The solution may be

### Determination of Tin

Tin can be deposited quantitatively from oxalate solutions, using stationary electrodes (p. 226). As the film of tin is difficult to remove from platinum, it is well to cover the cathode with a thin layer of copper.

The solution should contain not more than 0.3 gm. of tin, together with 10 gm. of solid potassium hydroxide and 10 gm. of oxalic acid crystals, per 100 ml. If this solution is not clear, boil it. Electrolyse at 65° C., using a current of 1 amp. The deposition will be complete after about six hours. The loss of water during the course of the experiment must be made good, and the cathode must be washed in cold water before the circuit is broken.

To test whether all the tin has been removed from the electrolyte, acidify a few drops with dilute sulphuric acid, destroy the oxalic acid by heating with a small excess of potassium permanganate, just decolorise with hydrogen peroxide, and add  $\text{H}_2\text{S}$ -water; a yellow colour or precipitate indicates the presence of tin.

### Determination of Lead

It is difficult to deposit lead in suitable form on a cathode, but easy to collect it as lead dioxide on an anode.

Weight out about 0.2 gm. of lead nitrate and dissolve the salt in water. Make up the solution with 20 ml. of concentrated nitric acid (sp. gr. 1.4) per 100 ml. of final electrolyte, and add 1 gm. of copper nitrate. Clean and weigh the rotating anode. Electrolyse at 60° C., using a current of about 2 amps. at 2 volts. Deposition will be complete in about half an hour. Wash and clean the anode in alcohol in the usual way, but dry it in an air-oven at 230° C. It is difficult to dehydrate the dioxide completely, and the results may be slightly high.

The coating of lead dioxide can be removed from the anode by dipping it into a beaker containing warm, dilute nitric acid to which a little cane sugar has been added.

*Note 1.* In accurate analysis, it is better to use the electrolytic method only as a means of separating lead from other metals.

*Note 2.* The electrolytic method is not suitable for the determination of lead in the presence of other metals.

Many other metals can be determined by electrodeposition. Of these, silver, iron and manganese are perhaps the most important, but the volumetric methods available are far superior both in speed and in accuracy.

## COLORIMETRIC ANALYSIS

Colorimetric analysis may be defined as analysis which depends upon a change in the intensity or shade of colour due to a chemical reaction. Many metals, non-metals and a large number of organic compounds can now be determined by this method, which is particularly suitable for small quantities. Colorimetry is often much more rapid than any other form of analysis. On the other hand, the method may lead to inaccurate results, because it depends on the matching of two colours. A person who has a poor perception of colour cannot hope to be very successful, and, on the other hand, persons who are extremely sensitive often fail. A colour, besides having a definite intensity, has a definite tint, and it is sometimes difficult to obtain two solutions of exactly the same tint. When the tints differ, the more sensitive the eye, the less satisfactory the method.

Four colorimetric processes are in general use. Of the four, the most important is the **balancing method**. Two tubes of the same dimensions and of colourless glass are taken. Solutions of the sample to be analysed and of reagents to develop the colour are put into the first. A standard solution of the compound of approximately the same concentration as the sample, together with the same quantities of the reagents, are placed in the second. When viewed from above, the solution which contains more of the active compound will have the more intense colour. On diluting the strong solution and again viewing from above, there will be little or no change in colour, because the quantity of the coloured substance in the field of view remains the same. As there may be a small change due to dissociation or to some other effect, it is essential that the standard solution has not only approximately the same concentration but also the same volume as that of the sample. The colours may be matched by withdrawing known volumes of the deeper-coloured solution. When the colours are the same, the same weights of compound are being viewed.

The withdrawal of solution from the tube is a clumsy and inaccurate process, but it is not necessary to withdraw it from the vessel, but only from the field of view. This can be done by inserting a smaller empty glass tube into the comparison tube, and viewing only the column of liquid between the bottom of the small tube and the bottom of the larger tube.

A less efficient method of balancing the colours by removing material from the field of view is to dilute the more deeply-coloured solution until the colours match when viewed horizontally through the tubes. This is the **method of dilution**.

The third method is the **method of duplication**. As in the balancing method, the sample is placed in a comparison tube and suitably treated. Into an exactly similar tube are put some water and the reagents. A standard solution is then run in from a burette until the colours, when viewed from above, are nearly the same. At this point, the two solutions are brought to the same volume and the colours made exactly the same by the addition of a few final drops of the standard. In theory this method is the best. In practice it often does not give accurate results, because the colours often change with time and are also influenced by the manner and order in which the reagents are added. Many of the coloured substances are colloidal. The size of the colloidal particles, which greatly

influences the intensity and tint, depends on the method of mixing. For example, the colour produced by taking 50 ml. of a standard and adding the reagents may be quite different from that obtained by taking the reagents and adding the 50 ml. of standard slowly from a burette.

The fourth method consists of making up a series of coloured standards to cover the range of concentration of the samples in a set of tubes. The colour of the sample is developed in a similar tube and the colours are matched by looking horizontally through the tubes. When a large number of determinations are to be carried through, this method is undoubtedly the most rapid and convenient. Unfortunately in only a few cases is it possible to make up a series of permanent standards, because either the colour fades or the colouring substance is precipitated.

Enough has been said to indicate that colorimetric analysis is by no means straightforward. Great care must be exercised and possible sources of error must always be kept in mind.

**Colorimeters.** Many forms, some of them very costly, have been devised, but for ordinary laboratory work simple apparatus only is required, such as a set of Nessler tubes (Fig. 101). These tubes should be of colourless glass, be of uniform bore, and have flat, polished bottoms which match optically. A test for this property is made by filling the tubes to the mark with distilled water. Tubes graduated at 50 ml. are of a convenient size, provided the height of the 50-ml. mark is about 20 cm. It is convenient to have all the tubes in a set of exactly the same dimensions. They should be kept in a Nessler rack (Fig. 101)—a test-tube rack painted a dull black with an opal-glass reflector mounted at the bottom, and with the base suitably bored so that light can be reflected up the tubes.

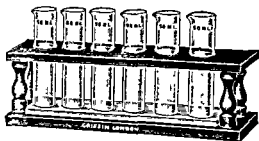


FIG. 101. NESSLER TUBES AND RACK.

Some form of colorimeter should also be available. A Duboseq-type colorimeter, such as shown in Fig. 102, is perhaps the most convenient. It consists of a metal stand which holds two glass cylinders with blackened sides and transparent bases. These cylinders are cup-shaped at the tops, and should be alike in all respects. In them are supported two smaller cylinders (which also have transparent bases and blackened sides), in such a way that the lower cylinders can both be moved up and down independently of one another by means of a screw motion, while the top cylinders are fixed. The length of this movement is measured on a scale on the side of the instrument.

At the base of the instrument is a source of light, rays from which are reflected equally up through both pairs of tubes by the inclined opal glass reflector. In the top of the instrument is an arrangement of prisms which enables the two disc-shaped fields representing the two cylinders to be seen as the two halves of the same circular field through the eyepiece at the top.

The coloured sample is placed in one of the wide-bottom cylinders and



a standard of similar concentration in the other, and the apparatus is then arranged so that the bottom of the top cylinder is just below the surface of whichever solution is least coloured. The other top cylinder is then moved until the two halves of the disc match exactly, when the concentration of the sample can be obtained from the formula :

$$CL = cl,$$

where  $C$  and  $c$  are the concentrations of the sample and standard, and  $L$  and  $l$  the heights of the respective columns of liquid. The tube containing

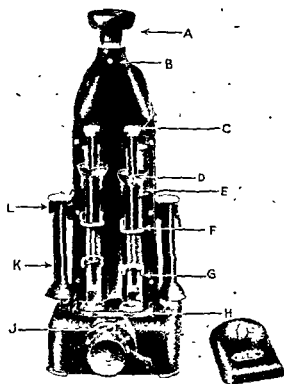


FIG. 102. OGAL DUBOSCQ-TYPE COLORIMETER.

A, eyepiece.  
C, plungers.

D, cups for solutions.  
H, reflector.

the least concentrated solution is then moved up some 3 or 4 cm. The height of the other column is then adjusted. In this way the average of three or four readings may be obtained from the same solutions.

This colorimeter thus allows solutions to be balanced by removing liquid from the field of view, though the liquid still remains in the vessels.

*Note.* For highly accurate results colorimeters of this type should be calibrated before use with the particular solutions which it is proposed to use in them. Thus, varying but known quantities of the substance to be determined are placed (with the reagent) in one of the vessels, and the resulting colours are matched by varying the height of the liquid column of a standard solution in the other vessel. A calibration graph may then be drawn relating the scale-reading on this side of the instrument with the concentration of substance under investigation, and this curve is used subsequently in making actual determinations. The advantage of this method is that it corrects for any optical inequalities

between the two sides of the colorimeter, as well as for any deviation in the law of simple proportionality between the colour intensity and the concentration of active constituent.

**Determination of Hydrogen Ion Concentration** (see also p. 205). An almost neutral water, such as ordinary tap-water, will serve as an example. Further information can be obtained from the books listed on p. 518.

Bromothymol blue, an indicator of  $P_H$  range 6.0, yellow, to 7.6, blue, is suitable. Use a solution made by dissolving 0.4 gm. of the indicator in 6.4 ml. of decinormal sodium hydroxide and diluting to 1 litre. Other suitable indicators are bromophenol red and phenol red; solutions are made by dissolving 0.4 gm. in 7.8 ml. of 0.1 N. NaOH and 0.2 gm. in 5.6 ml. of 0.1 N. NaOH, respectively, and diluting to 1 litre. Their  $P_H$  ranges are as follows: Bromophenol red, 5.2, yellow, to 6.8, red. Phenol red, 6.8, yellow, to 8.4, red.

Put 40 ml. of the water under test into a Nessler tube, and add 2 ml. of the indicator solution. Suppose that a  $P_H$  of about 7.0 is indicated (for instance, by a universal indicator, p. 495). Make up two buffer solutions of  $P_H$  6.8 and 7.2 respectively, in similar tubes, using one-fifth of the volumes of the reagent solutions recommended (Table, p. 495). Add 0.2 ml. of the indicator to each, and compare their colours with that of the water-sample. Suppose a "bracket" has been obtained, but that the colour of the sample corresponds more nearly with a  $P_H$  of 7.2. Make up a third buffer solution of  $P_H$  7.0 and compare again. From the comparison, judge whether the water-sample has a  $P_H$  of 7.0, 7.1, or 7.2.

The method described above is reasonably accurate when the water to be tested contains a considerable quantity of bicarbonate and, therefore, is itself buffered. With very pure water, however, there is a danger that the indicator will merely show its own natural  $P_H$ . To test whether this is in fact happening, repeat using either bromophenol red or phenol red, as seems most suitable. The natural  $P_H$  of these indicators is different from that of bromothymol blue, and if the  $P_H$  of the water in the two cases is shown to be the same, the water-sample must be sufficiently buffered.

It follows that the indicator method is unreliable for measuring the  $P_H$  of very pure water: the electrometric method (p. 205) must be used.

**Determination of Iron.** (a) *As Ferrocyanide.* When a solution of a ferric salt is treated with potassium ferrocyanide, an intensely blue precipitate of ferric ferrocyanide is produced. A colorimetric determination of iron can therefore be based on this reaction. It applies only to ferric iron, as the corresponding ferrous salt is colourless; and if the iron is present only in very small quantity (e.g., in water), because the colour is intense. If any iron is present in the ferrous state it may be converted to the ferric state by oxidation with hydrogen peroxide as described. The method can thus be used to determine ferric iron and total iron.

Take the solution to be tested for iron and concentrate it or dilute it until it contains about 2 milligrams of iron per litre. Make up a standard solution of iron containing about 20 milligrams of iron per litre by dissolving 0.14 gm. of ferrous ammonium sulphate in a little dilute sulphuric acid, precipitating with ammonia, oxidising the hydroxide by heating it with a few drops of hydrogen peroxide, and redissolving in sulphuric acid, and making up to 1 litre.

Take 50 ml. of the unknown solution and 5 ml. of the standard in two

tubes side by side. Dilute the standard to about 50 ml. To each add 1 ml. of concentrated hydrochloric acid, and 1 ml. of a solution of the potassium ferrocyanide containing 10 grm. of the salt per litre. Mix thoroughly, wait fifteen minutes and match the colours by diluting, or, better, by the method of balancing. The suspension of ferric ferrocyanide can be temporarily stabilised, if necessary, by the addition of 1 ml. of a 1 per cent. solution of gum arabic.

(b) *As Thiocyanate.* When a solution of ferric iron is treated with potassium thiocyanate under certain conditions, a complex, red-coloured ferric thiocyanate is produced. The colour is very sensitive to the presence of certain acids (e.g., nitric, oxalic, phosphoric), it fades on standing, and it is proportional to the iron content only over a limited range of iron concentrations. Good results can therefore only be obtained if the sample and the standard are alike in nearly all respects, and if they are treated in exactly the same way.

To determine the percentage of iron in commercial zinc by this method, make up a standard solution containing about 0.1 grm. of iron per litre by dissolving 0.7 grm. of ferrous ammonium sulphate in 10 ml. of dilute sulphuric acid and diluting to 1 litre.

Take 5 ml. of this solution in a small beaker, and add 2 grm. of iron-free zinc carbonate. Take 1 grm. of the zinc in a second beaker. Add a little water to the contents of each beaker and dissolve the solid in 8 ml. of concentrated HCl; add a few drops of  $\text{KMnO}_4$  solution, and boil to oxidise the iron. A permanent, faint pink colour on boiling indicates that oxidation is complete, and this is discharged by the addition of a few drops of HCl and boiling. Cool. Transfer to the comparison tubes and dilute to 50 ml. Add 2 ml. of ammonium thiocyanate solution made by dissolving 50 grm. of the crystals in 100 grm. of water. Mix well. Compare the colours by balancing. If the two solutions are not of approximately the same concentration, the determination must be repeated, using either more of the standard solution or of the zinc.

The ferric thiocyanate complex is insoluble in that mixture while many of the salts which bleach the colour and otherwise interfere are insoluble in that mixture.

The solution to be tested should contain about 0.02 milligram of iron in 5 ml. Develop the colour as described above, and shake the solution in a small separating funnel with successive 10-ml. volumes of a mixture containing equal volumes of amyl alcohol and ether. Pour off the red-coloured solvent-layer each time, and when this has only a pale brown shade, bulk the extracts and match them against those obtained from the standard solution of iron by the same procedure.

This method is suitable for the determination of iron in glass and porcelain. The finely-ground material should be fused with potassium hydrogen sulphate and then dissolved in water. A corresponding quantity of iron-free material similar in kind should also be fused under the same conditions, and added to the contents of the standard tube.

**Determination of Copper.** The order of the three methods described corresponds with an increasing degree of sensitivity.

(a) *By Ammonia.* The ammonium ion reacts with the cupric ion to give the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{++}$ , which has an intense blue colour. This is very sensitive to changes in temperature and to the presence of other ions. For example, the colour obtained by adding ammonia to a solution

of cupric chloride is quite different from that given by an equivalent of cupric nitrate. It is therefore safer to convert the copper to sulphate and to use copper sulphate as the standard. The quantity of copper taken should be such that the final solutions contain about 0.012 gm. per litre, *i.e.*, for the standard, take 10 ml. of a solution containing 0.12 gm. per litre for a final volume of 100 ml. Ammonia should be added to both the solutions until the blue colour is fully developed. Further dilution should be with 3 N. ammonia (concentrated ammonia diluted to five times its volume).

(b) *As Ferrocyanide.* When neutral solutions of potassium ferrocyanide and copper are mixed, a brown colour or a chocolate precipitate of cupric ferrocyanide  $\text{Cu}_2\text{FeC}_6\text{N}_6$ , is produced. If the correct conditions are chosen, 1 gm. of copper in 2,500 litres of water can be detected by this test.

To determine copper in burnt pyrites, for example, take 1 gm. of the pyrites in a small crucible, unglazed on the outside, and roast the ore over a Bunsen until all the sulphur has been removed. Cool, and digest the ore with concentrated HCl, adding a drop of nitric acid from time to time. Add 2 ml. of concentrated  $\text{H}_2\text{SO}_4$  and evaporate until most of the volatile acids have been removed. Cool. Dilute slightly, and add ammonia until alkaline. Remove the iron by filtration. Dissolve the precipitate in the least quantity of dilute sulphuric acid, reprecipitate with ammonia, filter, and add the runnings to the first filtrate. Boil this until excess ammonia has been removed. Cool and make up to a known volume, and take a suitable portion or, if the copper content of the pyrites is below 0.1 per cent., place all the solution in the first comparison tube.

The standard is made by dissolving a suitable quantity of pure copper sulphate in water, adding ammonia until alkaline, and boiling off the excess of ammonia, in parallel with the assay; it should contain 0.1 gm. of copper per litre.

Take 5 ml. each of the standard and of the solution of sample. Add water until the volumes of each are the same, conveniently 45 ml. To each add 5 ml. of a saturated solution of ammonium chloride, 2 drops of concentrated hydrochloric acid and 5 drops of a 1 per cent. solution of potassium ferrocyanide. Mix well, and match in a colorimeter. It is important to add the ferrocyanide to both solutions at the same time, because the copper complex may coagulate. Poor results are obtained by adding the standard from a burette. If no colorimeter is available, dilute the more concentrated of the solutions with water until the colours, viewed horizontally through the cylinder, match. If the solution is alkaline, the colour will fade.

If the copper content of water is to be determined, any lead also present will give a white turbidity in the liquid due to insoluble lead ferrocyanide; in this event add a similar quantity of lead, as a solution of lead nitrate, to the standard. Iron, if present, must be removed by ammonia (see above).

(c) *By Sodium Diethyldithiocarbamate*  $[\text{N}(\text{C}_2\text{H}_5)_2\cdot\text{CS}_2\cdot\text{Na}]$ . When this reagent is added to an acidic, neutral, or alkaline solution of copper, a golden-brown colour is produced. The test will determine less than 1 part of copper in 100 million parts of water. It is of particular use for determining copper in drinking water; or in solutions from which nearly

all the copper has been removed by electrodeposition (p. 229). Interference by zinc is negligible, provided the solution is strongly ammoniacal; iron in small quantity does not interfere, provided that a considerable quantity of citric acid is present. The interference of other metals can be avoided by taking advantage of the fact that the coloured copper compound is soluble in carbon tetrachloride.

The standard solution should contain about 10 milligrams of copper per litre. Such a solution can be made by dissolving 0.393 gm. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water and diluting to 100 ml., and by taking 10 ml. of this solution and diluting to 1 litre. Use a 0.1 per cent. aqueous solution of the reagent. This is somewhat unstable, but will keep for several weeks if stored in the dark.

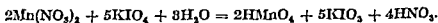
Normally, make the solution slightly ammoniacal. If iron is present, oxidise it, add 2 gm. of citric acid, and make the solution alkaline; if zinc is present, make the solution strongly ammoniacal. Add this solution to 10 ml. of the reagent solution, dilute to about 50 ml. if necessary, and balance against a standard copper solution which has been treated in exactly the same way.

*The Extraction Method* may be used when a considerable quantity of ferric iron is present or when the simple method fails to give a satisfactory result, as when other interfering elements are present or when the quantity of copper to be determined is extremely small.

Add 2 gm. of citric acid to the sample and to the standard, and dilute each to about 40 ml. Add 0.880 ammonia diluted with its own volume of water, until the  $P_H$  values of the solutions are greater than 9. Test this, using phenolphthalein on a spot-plate. The indicator should turn definitely red. Bring the volume of each solution to 70 ml. and add 10 ml. of the dithiocarbamate reagent. Mix well and then extract at once with at least four successive portions of 2.5 ml. of carbon tetrachloride. Transfer the extractions to small tubes and dilute to 20 ml. with carbon tetrachloride. Compare the colours.

**Determination of Manganese.** The metal is oxidised to a permanganate by sodium bismuthate, silver persulphate or sodium periodate. The last of these reagents gives the best results.

(a) *Periodate.*



The sample to be analysed should be free from reducing agents and from chlorides. If it contains an element, other than manganese or iron, which gives a coloured ion, an equivalent quantity of that element should be added to the blank. The final solution in the comparison tube should contain about 2 milligrams of manganese in 100 ml. of solution.

Dissolve the material in a mixture of 15 ml. of concentrated  $\text{H}_2\text{SO}_4$  and 20 ml. of concentrated  $\text{HNO}_3$ . The solution should be boiled to make certain that all reducing agents are removed. If the material contains carbides, e.g., in steel, it is best to add a little solid ammonium persulphate to the boiling nitric acid solution to ensure complete oxidation. If the solution contains iron, add 10 ml. of syrupy phosphoric acid to bleach the colour due to the iron. If chloride is present the acid solution must be evaporated until the chlorine has been removed.

Dilute to 100 ml. and add 0.4 gm. of sodium periodate to the boiling solution. Boil for one minute, immerse in boiling water for ten minutes, cool, dilute to a suitable volume and compare the colour with that of manganese standards prepared by the same method; or balance against one standard. Thus,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , may be used; or preferably, a standard solution of potassium permanganate may be reduced with a few drops of a solution of sulphur dioxide (1 ml. of centinormal  $\text{KMnO}_4$  contains 0.11 milligram of manganese). As permanganic acid is comparatively stable in presence of excess of periodate, standards can be kept in stoppered vessels in the dark for three or four months. If a large number of analyses is to be carried through, it is convenient, therefore, to make up a set of tubes each containing a different concentration of manganese.

(b) *Persulphate. Rapid Method for Manganese in Steel.* A standard steel similar in composition to the one to be analysed should be available. Take 0.1 gm. of the standard and 0.1 gm. of the sample. Dissolve in 5 ml. of  $\text{HNO}_3$  (sp. gr. 1.2) in test-tubes placed in boiling water in a bath. Add to each 7 ml. of centinormal silver nitrate and 0.7 gm. of ammonium persulphate in 2 ml. of water. Heat in the boiling water until there is a brisk evolution of oxygen. Remove, and cool quickly under the tap. Transfer to the comparison tubes, dilute suitably, and balance. As the operation is speedy and as the oxidation with persulphate even in the presence of the catalyst is unreliable, it is as well to carry out each analysis in duplicate, using two standards and two samples. If the colours of each pair are nearly alike, the two standards and the two samples may be mixed before matching. If they are not alike, another sample must be dissolved and oxidised under slightly different conditions. The colour of the permanganate may fade rapidly.

**Determination of Nickel by Dimethyl Glyoxime.** The use of this reagent for the gravimetric determination of nickel was dealt with on p. 62. If, however, the amount of nickel is small, a reddish-brown coloration may be produced instead of the red precipitate, and this enables 0.2 milligram of nickel to be determined colorimetrically. The method may be used in the presence of cobalt, but if much of the latter is present, special precautions to eliminate its effect must be taken.

Make the solution to be analysed, which should contain 0.1 to 0.01 milligram of nickel, slightly ammoniacal, dilute to 100 ml., and stir in 2 ml. of a saturated solution of dimethyl glyoxime in alcohol. Add 1 ml. of a 5 per cent. solution of sodium hypochlorite, and match the colour against that produced from a standard (which should be developed simultaneously) after three minutes.

A standard can be made conveniently by dissolving nickel ammonium sulphate,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , in water. A concentration of 0.673 gm. of this salt per litre gives 0.1 milligram of nickel per millilitre.

**Determination of Aluminium by Aluminon.** Aluminon is ammonium aurine tricarboxylate, a dye which can form brilliantly-coloured lakes with several metals. The lake with aluminium is bright red, and it enables 0.002 milligram of aluminium to be detected and 0.05 milligram to be determined. The optimum quantity for determination is about 0.3

milligram. The reaction is so sensitive that great care must be exercised to prevent contamination from the vessels used. So far as possible, Pyrex glass should be employed. Chromium, the alkaline earths, phosphates and iron are the most important of the substances which interfere, but, with the exception of iron, their interference in the presence of ammonium carbonate is so small that it is seldom necessary to remove them. Iron must either be removed or an equivalent quantity of it be added to the standard aluminium solution.

Ammonium carbonate decreases the sensitivity of the reagent and, in the absence of interfering substances, it is best to use a solution of  $P_H$  0.3. This may be obtained by adding a concentrated solution of ammonium acetate to the aluminium solution after it has been acidified with hydrochloric acid. Sometimes the lake shows a tendency to precipitate immediately. This can be prevented by the addition of a little gum arabic solution.

The determination of aluminium in water is described below.

*Without Removal of Iron.* To a suitable volume of the water, say 100 ml., add 2 ml. of dilute hydrochloric acid, evaporate to dryness, and ignite at a dull-red heat for a short time. Cool. Digest with 5 ml. of water which has been acidified with a few drops of dilute hydrochloric acid, and remove the silica by filtration. Transfer to a Nessler tube and place suitable, known quantities of aluminium in a set of similar tubes, together with that weight of iron which a previous estimate has shown to be present in the water. A solution containing 0.05 milligram of aluminium per millilitre may be prepared by dissolving 0.879 gm. of ammonium alum in a little water acidified with hydrochloric acid, and diluting to 1 litre. Take, say, 2, 4, 6, 8 ml. of such a solution in four tubes. Bring these standards and the solution for analyses to the same volume, say 20 ml. Add to each, in the following order, 5 ml. of dilute hydrochloric acid, 5 ml. of a 25 per cent. solution of ammonium acetate and 5 ml. of a 0.1 per cent. aqueous solution of the reagent. After five minutes, add 5 ml. of dilute ammonium hydroxide and 10 ml. of a solution containing 200 gm. of ammonium carbonate per litre. Mix well. Compare the colours after fifteen minutes, but before one hour.

*With Removal of Iron.* Proceed as before. Add concentrated nitric acid or bromine water to the filtrate and washings from the silica, and boil to oxidise the solution. Remove the excess of bromine by evaporation. Dilute to 100 ml. and, to precipitate the iron and aluminium, add dilute ammonia to the hot solution until it is neutral to methyl red. Filter while hot. Dissolve the precipitate in a small volume of 25 per cent. nitric acid, washing the paper with a little hot water. Make this solution strongly alkaline with a 25 per cent. solution of sodium hydroxide, which must be free from aluminium. Boil and filter. Wash with hot water, and then neutralise filtrate and washings with dilute hydrochloric acid (litmus paper), adding 1 ml. of this acid in excess. Cool. Determine the aluminium as described above. If the colour develops fully after the addition of the ammonium acetate and the reagent, the addition of ammonia and ammonium carbonate becomes unnecessary.

**Determination of Lead.** Advantage is taken of the fact that when a soluble sulphide is added to a solution of lead in the presence of gum

arabic, the lead sulphide is not precipitated, but forms a brown colloidal solution. The sample to be analysed should contain not more than 0.25 milligram and not less than 0.005 milligram of lead. The standard is conveniently made by dissolving lead nitrate crystals in distilled water and diluting to 1 litre. A suitable concentration is 0.02 milligram of lead per millilitre (0.1598 gm. of lead nitrate per litre; 100 ml. of this solution are taken and diluted to 500 ml.). To a suitable volume of the solution in HCl add 2 ml. of saturated ammonium citrate solution (to both stabilise the final colour and minimise interference by phosphates). Then make the solution ammoniacal, and add about 0.2 gm. of solid KCN (to minimise interference by Fe and Cu). Dilute to 50 ml., and add 3 ml. of a fresh 2 per cent. solution of sodium sulphide. Mix well. Make up the comparison tube in exactly the same way, first using 10 ml. of the standard lead solution and taking care that all the solutions are at the same temperature. Balance the colours immediately.

*Lead in Drinking Water* may be determined with some accuracy, in the absence of iron and copper, by the addition of 2 ml. of a 10 per cent. solution of acetic acid and 1 ml. of hydrogen sulphide solution to 100 ml. of the sample, the standard being treated similarly.

The colour of the lead sulphide is influenced by the presence of certain radicals, for example, citrates, tartrates and ammonium salts. Care must therefore be taken that if these are present, suitable additions are made to the standard lead solution, as described above. The ammonium chloride deepens and stabilises the colour of colloidal lead sulphide. Some is produced by neutralisation, but more may be added to both sample and standard.

**"Dithizone" Separation.** Lead may be separated from the heavy metals, including iron but excepting bismuth, by extraction with a solution of diphenyl thiocarbazon ( "dithizone" ) in chloroform in the presence of alkali and a cyanide.

separated extract with 10 ml. of water, mix the three chloroform extracts, and remove the solvent by distillation.

Destroy the organic matter in the lead-dithizone complex remaining by heating with 1 ml. of sulphuric acid until white fumes result and then add

**Determination of Bismuth as Oxide.** Bismuth salts form a yellow-coloured complex, possibly  $\text{BiI}_3 \cdot 3\text{KI}$ , with potassium iodide; this enables 0.01 milligram of bismuth to be detected.

Make a standard solution by dissolving 0.1 gm. of bismuth in nitric acid and diluting to 1 litre, taking care that sufficient nitric acid to prevent the precipitation of bismuth oxynitrate is present. The concentration of nitric acid must be known.

For the determination of bismuth in copper, dissolve a weight of the copper equivalent to 2 milligrams of Bi in 50 per cent. nitric acid. Dilute with water and add bench sodium carbonate until a slight, permanent precipitate forms. Add 1 ml. of the carbonate in excess. Boil for five



minutes. Filter, and wash with water. Dissolve the precipitate, which will contain all the bismuth, in the least possible quantity of 50 per cent. nitric acid, and remove any copper by reprecipitating the bismuth with 0.880 ammonia diluted with its own volume of water. Collect the precipitate, wash it with water, and dissolve it in a small, known volume of the nitric acid. Transfer to a colorimeter tube and place 20 ml. of the standard in a second tube. Dilute each solution to about 90 ml., making sure that each tube contains the same quantity of nitric acid. Add, to each, 10 drops of a solution of sulphur dioxide, made by adding 1 volume of saturated solution to 2 volumes of water, and 5 ml. of a 20 per cent. solution of potassium iodide. Dilute to 100 ml., and match.

✓ **Determination of Titanium in Clay or Ore.** When hydrogen peroxide is added to an acid solution containing titanium, an orange-red or yellow colour in concentrated or dilute solutions, respectively, is produced. This is probably due to the presence of hexavalent titanium.

Weigh out accurately enough of the sample to give 0.01 to 0.05 gm. of titanium. Mix it thoroughly with eight times its weight of sodium peroxide and heat it in an iron crucible until all is in solution. Many titanium ores are resistant to sodium peroxide, and therefore they must first be ground extremely finely. Cool the fused mass and dissolve it in 200 ml. of water. Add 8 ml. of concentrated  $H_2SO_4$ , followed by 3 ml. of syrupy phosphoric acid to eliminate the colour due to iron; however, this also reduces to some extent the intensity of the colour of the titanium solution. Unless very accurate results are required, there is no need to filter. Transfer the solution to the comparison tube and balance against a standard.

The standard solution of titanium is an approximately decinormal solution of titanous chloride. Standardise it volumetrically (p. 185), dilute it ten times, and take a convenient quantity for the colorimetric test. Develop the colour by adding 2 ml. of 3 per cent. hydrogen peroxide to the contents of the tube, first making sure that the concentrations of sulphuric and phosphoric acids in this tube and in the sample-tube are the same.

Before carrying through a large number of determinations of titanium, it is convenient to prepare a series of standards, preferably from methyl orange. Dissolve 1 gm. of methyl orange in 500 ml. of water. Take 50 ml. of this solution and dilute to 1 litre. Using this dilute solution, make up a series of standards to cover the required colour range. Standardise the standards against known quantities of titanium. The colours are similar in tint, and the methyl orange colour is more permanent than that of the titanium. ✓

**Determination of Antimony.** This method has the special advantage that it can be used in the presence of tin and arsenic; sensitiveness 0.05 milligram Sb. Add to a Nessler cylinder in the order stated: 10 ml. of 1 per cent. gum arabic solution, 5 ml. of 20 per cent. KI solution, 1 ml. of a saturated solution of pyridine in water, 1 ml. of 20 per cent. sulphurous acid (water saturated with sulphur dioxide and diluted 10-fold) and 60 ml. of dilute (1:3) sulphuric acid. Mix, add 25 ml. of the sample, and match the resulting orange-yellow colour against that obtained similarly

from a standard solution of tartar emetic (2.667 gm. in 1 litre of dilute hydrochloric acid; 1 ml.  $\equiv$  1 milligram of Sb).

**Determination of Nitrates by Diphenylamine Sulphonic Acid.** When this reagent is treated with a trace of nitric acid, a complex reaction takes place and an intense blue colour is produced. Nitrates interfere and must be removed by boiling with ammonium chloride. Urea, which itself interferes, must not be used to destroy the nitrites.

Prepare a series of standards to cover the range from 0.0001 to 0.005 milligram of nitrogen by putting suitable quantities of potassium nitrate into a series of tubes. A solution containing 0.0001 milligram of nitrogen per millilitre may be made by dissolving 0.072 gm. of potassium nitrate in water and diluting to 1 litre, and diluting 10 ml. of this solution to 1 litre. To each standard and to the sample add 10 ml. of a 1 per cent. solution of potassium chloride, dilute each to 100 ml. and add 10 ml. of concentrated sulphuric acid. Cool in water and stir. Add to each 2 drops of a solution containing about 1.5 gm. of sodium diphenylamine sulphonate per litre. Stir, and match the colours.

As the intensity of the colour is not related simply to the concentration of the nitrate, it is well to repeat the determination, using standards covering closer intervals. In this event, a new sample must also be prepared simultaneously, because the intensity of the colour varies to a considerable extent with time.

The method for the determination of nitrates in drinking-water by phenoldisulphonic acid is given on p. 360.

**Determination of Nitrites.** Advantage is taken of the fact that when nitrous acid is allowed to react with a soluble iodide, free iodine is produced and colours starch solution blue.

*The Iodide-Starch Solution* is best prepared as follows: Boil together 5 gm. of starch, 20 gm. of stannous chloride and 100 ml. of water for some hours, keeping the volume constant by adding water to replace that lost by evaporation. Then add 2 gm. of zinc iodide, and dilute to about 1 litre. Filter, or better, put aside for some days when any solid will have settled and the clear solution can be drawn off as needed. Make up a solution of sodium nitrite containing about 0.5 gm. of the salt per litre and standardise it against potassium permanganate (p. 160). To obtain a solution suitable for colorimetric analysis, dilute the standard 100 times. One millilitre of the very dilute solution will contain about 0.001 milligram of nitrogen.

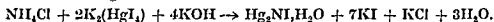
Take 50 ml. of the sample in a comparison tube, together with a suitable volume of the standard, diluted to 50 ml., in the second tube. Add 2 ml. of 1:3  $\text{H}_2\text{SO}_4$  and 4 ml. of reagent to each. Mix thoroughly. Set aside for fifteen minutes and match the colours.

A quantity of 0.0001 gm. of nitrogen as nitrite can be detected in 50 ml. by this method. It must be remembered that the colour develops more rapidly in bright than in dull light, that it becomes more intense on standing, and that the determination can only be carried out satisfactorily in an atmosphere free from nitrous fumes and chlorine.

Nitrite in drinking-water may be determined colorimetrically by the sulfanilic acid and  $\alpha$ -naphthylamine method (p. 357).

Alternatively the nitrates are first determined. Then the ammonia content is found by Nessler's method (see below). Finally, the nitrates and nitrites are reduced to ammonia (p. 350) and This reduction can also be carried out 00 ml. of the sample, to which have been added 10 ml. of potassium hydroxide. The vessel should be nearly closed and left overnight. The quantity of ammonia carried away by the hydrogen is very small. If necessary it can be trapped in water. If the reduced solution is clear, it can be treated directly with Nessler's solution. If it is cloudy, two-thirds of the liquid must be distilled off and collected. All the ammonia will be in this fraction.

**Determination of Ammonia.** When an alkaline solution of potassium mercuric iodide, Nessler's reagent, is allowed to react with ammonia, dimercuric ammonium iodide, which imparts a yellow or brown colour to the solution, is formed :



Nessler's reagent is prepared as described on p. 351, where the method is dealt with fully. The sample should be 100 ml. in volume. Develop the colour by adding 3 ml. of Nessler's reagent, and match against a suitable quantity of the standard diluted to 100 ml. and treated simultaneously with 3 ml. of the reagent.

It frequently happens that the sample to be tested for ammonia contains calcium and magnesium, which are precipitated by the reagent. They must therefore be retained in solution by adding 3 ml. of 50 per cent. Rochelle salt, sodium potassium tartrate, to 100 ml. of sample. This, of course, should be added before the Nessler solution. As the Rochelle salt solution is somewhat unstable, it is usual to preserve it by adding 50 ml. of Nessler reagent to each litre. Unless the solution of ammonia is very dilute, the mercury salt is precipitated and it is probable that the colour of very dilute solutions is due to the presence of the iodide in colloidal solution. Despite this fact, the colour is comparatively permanent, and it is satisfactory to make up a series of permanent standards if many analyses are to be carried through.

An objection to this method of determining ammonia is its extreme delicacy. Ammonium chloride is a frequent impurity in the air of a laboratory, and it cannot be too strongly emphasised that suitable precautions must be taken to prevent contamination of the samples and standards by absorption of ammonia. All distilled water to be used for dilution should first be tested by Nessler's reagent. Ammonia is often found even in freshly-distilled water. Suitable water can be prepared by adding about 1 gm. of potassium permanganate and 1 gm. of sodium carbonate to 500 ml. of the contaminated liquid and distilling. The first 100 ml. of the distillate should be rejected.

*The determination of ammonia in water by the standard method is given in full on pp. 350-354.*

**Determination of Phosphates.** To the solution to be tested add, in succession, 1 ml. each of a mixture of 65 ml. of sulphuric acid in 450 ml. of water; a fresh solution prepared by mixing 200 ml. each of 8.75 per

cent. ammonium molybdate solution (prepared in the cold) and 5.25 per cent. sulphuric acid and diluting to 500 ml. ; and a fresh solution prepared by adding 0.3 ml. of sulphuric acid to 500 ml. of a 1 per cent. solution of hydroquinone. After five minutes a green colour develops ; then add rapidly 2 ml. of a solution of 100 grm. of anhydrous sodium carbonate and 24 grm. of sodium sulphite in 500 ml. of water, mix, and match the blue colour as rapidly as possible against that produced from a 0.01390 per cent. solution of  $\text{HNa}_2\text{PO}_4$  (equivalent to 100 parts per million of  $\text{PO}_4^{--}$ ).

**Determination of Fluorides.** Fluorides have a bleaching effect on the orange colour produced by the reaction of titanium salts with hydrogen peroxide (p. 244) ; under the conditions specified this effect is proportional to the fluoride content.

If necessary remove iron and aluminium by fusing the sample with a 5-fold weight of a mixture of sodium and potassium carbonates, and heat an extract of the melt with 2 grm. of  $(\text{NH}_4)_2\text{CO}_3$  on a water-bath for twenty minutes. Cool, filter, evaporate to 25 ml., filter again, and just neutralise the filtrate with 6N.  $\text{H}_2\text{SO}_4$ . Shake to liberate the  $\text{CO}_2$ , and for each 0.01 grm. of  $\text{F}^-$  believed to be present add 12 ml. of the  $\text{H}_2\text{SO}_4$  in excess. Dilute to a convenient volume, and to an aliquot portion containing 1 to 2 milligrams of  $\text{F}^-$  add 20 ml. of a solution of  $\text{TiO}_2$  in  $\text{H}_2\text{SO}_4$  (1 ml.  $\equiv$  1 milligram of  $\text{TiO}_2$ ) and 3 ml. of 3 per cent.  $\text{H}_2\text{O}_2$  ; dilute to 100 ml. Match the colour against that obtained by adding known quantities of a fluoride to a similar reaction-mixture ; 1 milligram of  $\text{F}^-$  bleaches 19 per cent. of the Ti present.  $\leftarrow$

**Determination of Carbon in Steel.** This method is very rapid, but the results may be 20 per cent. in error. A yellow colour due to the nitration of an organic compound is produced when steel is dissolved in nitric acid (sp. gr. 1.2). The depth of the colour depends on the original condition of the carbon in the steel. Thus, if the carbon is present as cementite, the colour is produced fully ; if in solid solution, only in part ; and if as graphite, not at all. The colour is changed by the presence of many of the elements commonly found in steel, namely nickel, chromium and manganese. Moreover, the intensity is not proportional to the carbon content. For these reasons it is important to use a standard steel which is similar in composition and heat-treatment to the sample which is to be analysed. The carbon in the standard may be determined by the dry combustion method (p. 304).

Dissolve 0.15 grm. of the steel and of the standard, in the form of fine drillings, in 3 ml. of the nitric acid, in test-tubes. When the violent action has ceased, heat the tubes in a water-bath until any brown flocks have disappeared. Cool under the tap. Transfer to a pair of small, graduated comparison-tubes and dilute the deeper-coloured solution until the colours when viewed through the tubes are the same.

**Determination of Arsenic.** This determination is of particular importance because the Sale of Food and Drugs Act imposes limits on the amounts of arsenic which may be present in certain commodities. The two methods in common use both depend on the fact that when hydrogen is liberated in the presence of a soluble arsenic compound, the latter is converted into

the gas arsine ( $\text{AsH}_3$ ), which can be removed from the apparatus in this form in the current of hydrogen. In the up-to-date form of the Marsh-Berzelius test the hydrogen is produced electrolytically, and the gases evolved are passed through a heated tube. The stain of arsenic deposited by the decomposition of the arsine is matched against stains produced from known amounts of arsenic in a similar way.

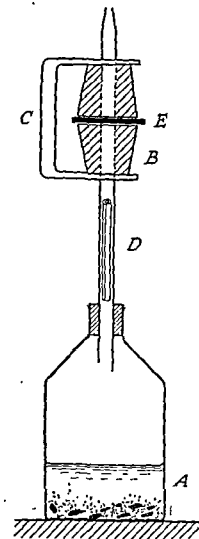


FIG. 103. GUTZEIT ARSENIC APPARATUS.

As the other method (the Gutzeit test) requires less elaborate apparatus, and in its standardised form is accepted officially for many purposes, it is chosen for description here. In this case the gas is produced by the action of zinc on an acid and is passed through a mercuric bromide paper, on which the  $\text{AsH}_3$  leaves a brown stain. Although therefore, this is essentially a colorimetric method, it differs in that coloured stains on paper, and not coloured solutions, are matched.

The apparatus (Fig. 103) consists of a 120-ml. wide-mouthed bottle (A) fitted with a rubber bung carrying a thick-walled tube about 15 cm. long, the top end of which is ground flat and is flush with the upper end of a hole in a rubber bung (B); a similar bung and tube is held in contact with it by means of a clip (C), in such a way that the bore of the two tubes is continuous. D is a roll of filter-paper ( $4 \times 10$  cm.) which has been soaked in 5 per cent. lead acetate solution and dried; it traps  $\text{H}_2\text{S}$  and other volatile sulphides. A solution of the sample in dilute  $\text{H}_2\text{SO}_4$  (free from  $\text{HNO}_3$ ) is placed in the bottle, 10 grm. of granulated zinc and a little stannous chloride are added, and the cork is quickly replaced. Between the rubber bungs should be sandwiched a test-paper (E), prepared by soaking, a dry filter-paper in a 1.5 per cent. solution of  $\text{HgBr}_2$  in 95 per cent. alcohol, and allowing it to dry in warm air; this should be prepared shortly before it is required.

Under these conditions the hydrogen liberated by the zinc and acid reduces the arsenic present to the gas arsine ( $\text{AsH}_3$ ), which is carried off with it and through the paper (E) on which it leaves a brownish stain. After thirty to forty minutes the stain may be compared with that obtained under similar conditions from solutions containing 0.001 to 0.020 milligram (or other convenient quantities) of  $\text{As}_2\text{O}_3$ . These are prepared from dilutions of a solution of 1 grm.  $\text{As}_2\text{O}_3$  in 25 ml. of 20 per cent.  $\text{NaOH}$ , which is then neutralised with  $\text{H}_2\text{SO}_4$  and diluted to 1 litre with 1 per cent.  $\text{H}_2\text{SO}_4$ ; this solution is further diluted with acid until 1 ml. contains 0.001 milligram of  $\text{As}_2\text{O}_3$ .

Reagents sold as "arsenic-free" should be used for the test, and it is advisable to make allowance for a blank test in which the same amounts of reagents (including the sulphuric and nitric acids) are used. The stains may be preserved by drying the test-paper at  $105^{\circ}\text{C}$ . and dipping it in molten paraffin wax; standard stains should be stored in a desiccator over phosphorus pentoxide in the dark.

### NEPHELOMETRIC ANALYSIS

The term "nephel" means a cloud, and nephelometry is the measurement of cloudiness or turbidity. It is analogous to colorimetry in that it depends on the formation of a turbidity as the result of a chemical action, and this is measured by matching it against turbidities produced from known quantities of a standard solution of the substance concerned. Incidentally, the method was used some fifty years ago by T. W. Richards in some of his classical atomic weight determinations. As will be shown, such measurements may be made easily and rapidly; and since a small amount of substance usually produces a relatively pronounced turbidity, the method is particularly rapid, convenient and sensitive.

In describing how these measurements may be made, it is first necessary to consider briefly the fundamental effect on light of the fine particles which constitute a turbidity. There are two possible methods of measuring turbidities. The obvious one is to measure the height of the column of turbid liquid necessary just to obscure a given mark (*e.g.*, a black spot on a white tile). This is carried out by supporting a glass cylinder (*e.g.*, a Nessler cylinder) over the spot, and pouring in the turbid liquid until the spot just becomes invisible; the volume, or height, of the column of liquid is then measured. The method must, of course, be "calibrated" by measuring the corresponding heights for solutions of known turbidity (*i.e.*, containing known concentrations of the substance producing the turbidity). The calibration curve relating concentration and height (or volume) may then be used to measure concentrations of unknown magnitudes. This "extinction method," as it is called, suffers from the disadvantage that it depends upon the transmission of light through the turbidity. It is, therefore, not particularly sensitive as a method of measurement, especially in view of the limitations of the human eye, and it is further upset if the solution is at all coloured, as the colour will absorb transmitted light quite independently of the turbidity. Fortunately, the sensitiveness can be increased considerably by measuring the amount of light scattered by the particles, and it is methods such as this which have facilitated the application of nephelometric methods.

**Apparatus.** The colorimeter described on p. 236 may readily be adapted to the practical realisation of this latter principle. The vessels containing the solutions however, have opaque bases and transparent sides and are illuminated from the side; colorimetry vessels on the other hand, have opaque sides and transparent bases, and are illuminated through the latter. In the operation of the nephelometer, the amount of light reaching the eye will depend on the number of scattering particles in the solution which are exposed to the light, and this in turn will depend partly on the concentration of the reacting substance from which they are derived, and partly on the height of the column of liquid viewed; the latter is therefore

varied by altering the height of the plunger exactly as in colorimetry. Thus, if the turbidity produced from the solution to be analysed is in one vessel, and that from a stronger standard solution of the same substance is in the other, the plunger in the latter may be lowered until a match is obtained when, under ideal conditions, the heights of liquid being viewed will be inversely proportional to the respective concentrations; the unknown concentration may therefore, then be found by proportion.

In practice however, it is safer to calibrate the apparatus against solutions of known strength as described under Colorimetry (p. 236), and to read off the results from the curve so obtained. The use of universal suspensions, or even of plates of frosted glass which will serve as permanent standards for reactions of all types, has also been suggested, but these are not to be recommended as they fail to reproduce the subtleties of all types of opalescence.

Photo-electric methods in which the turbidity is measured in terms of the thickness of liquid necessary to cut off the activating light from a photo-electric cell, have proved very useful, as they eliminate the human error inherent in work of this kind. A particularly efficient arrangement comprises two photo-electric cells arranged in electrical opposition, in such a way that when they are equally illuminated no current passes in the circuit. If the two sources of illumination are the rays from a common point after transmission or scattering by the sample and standard, respectively, then by adjusting the strength of the latter until no current passes, the strength of the former may be found.

**Examples.** The method is widely used for control purposes in industry, e.g., for measuring changes in the suspended solids content of water, but the following are examples purely of analytical interest :

**Silver or Chlorides.** For chlorides, place approximately equivalent amounts of the solution to be tested and the standard (1 ml.  $\equiv$  0.1 milligram of Cl) in the two matching vessels, and add an 8-fold excess of  $\text{HNO}_3$ ; match after four minutes, keeping the solutions in the dark in the interval. The best results (error, about 1 per cent.) are obtained with 0.000005 N. solutions, but in such cases thirty minutes should elapse before matching. If the Nessler method is used, matching is best carried out over a tile, half of which is white and half blackened, so that the boundary between the black and white portions intersects the circular field of the base of the cylinder.

**Zinc** is conveniently determined as ferrocyanide. The procedure is described on p. 368 in connection with water analysis.

**Aluminium.** The reagent is 1 ml. of a 5 per cent. solution of cupferron which is added to 25 ml. of a solution containing 0.15 to 30 milligrams of aluminium per litre. The matching error is about 2 per cent., but the colours produced by iron and copper with this reagent increase this error, and these metals should be removed if present.

**Magnesium and Phosphates** are bracketed together because the method for the latter may also be used for the former. This magnesium is very conveniently separated as magnesium ammonium phosphate, the phosphate in the resulting precipitate being determined as follows: To a mixture of 30 ml. of water, 5 ml. of 0.5 N. hydrochloric acid and 5 ml. of reagent (see below) are added 10 ml. of the test solution, which should previously

have been neutralised with ammonium hydroxide if necessary, and filtered. The reagent is prepared by mixing 150 ml. of a 2 per cent. solution of strychnine sulphate with a solution of 150 gm. of sodium molybdate in a mixture of 250 ml. of water and 100 ml. of 50 per cent. hydrochloric acid; the mixture is shaken, and filtered on the next day. The sensitiveness of the method is 0.5 part per million of phosphorus.

*Proteins* may be included as an example of the application of the method in organic chemistry, and because the usual methods of analysis are very lengthy and complicated. Where however a suitable precipitant is available, a determination may be made in thirty minutes, and the error is of the order of less than 10 parts per million.

Edestin, which is precipitated by 9 per cent. NaCl solution, is a convenient example. To prepare the standard solution make 0.1 gm. of edestin into a paste with water, add 3 ml. of 0.1 N. HCl, filter into a 100-ml. flask, add 1 drop of chloroform and dilute to the mark. Dilute this solution 20 times before use, to obtain a 0.005 per cent. solution. Make the determination by adding the NaCl reagent, drop by drop from a burette, to a solution of the sample of about 0.001 per cent. concentration and mix by a rotary motion during the addition; match against the standard, treated similarly.

*The Activity of Enzymes* which digest proteins (e.g., trypsin and pepsin) is estimated by determining nephelometrically the protein content of a solution before and after the enzyme has acted upon it. Other nephelometric methods are described by Yoe (p. 519).

## OTHER METHODS OF ANALYSIS

The purpose of this section is to draw the student's attention to other methods of quantitative analysis which cannot be described fully in this book.

**Micro-Chemical Methods.** The saving of time, space and materials brought about by the introduction of these methods makes them of the greatest importance, particularly in ultimate organic analysis. Thus a determination of carbon and hydrogen in a compound by the ordinary methods usually takes rather more than two hours, but the micro-methods will give results in about quarter of that time. Most of these methods, which involve quantities of the order of 10 to 100 milligrams, are similar in principle to the corresponding normal macro-methods, with modifications in technique appropriate to the smaller quantities involved. It has been thought desirable, therefore, to describe the

t  
t  
volumetric apparatus involved. Those methods described are recommended as very useful exercises in analytical technique for students, but they only touch the fringe of a wide subject; for further information consult the English translation of Pregl's *Quantitative Organic Microanalysis*, and Mitchell's *Recent Advances in Analytical Chemistry*.

**Spectrographic Analysis.** An arc is struck, or a series of sparks is passed, between two electrodes of the metal to be examined; or the material is contained in a little cup cut in the end of a graphite rod, and



an arc is struck between this and a second carbon electrode. The resulting light is passed through a quartz prism and the spectrum is photographed. The determination is made by comparing the intensities of the lines produced by the impurities with those due to the principal metal; or by photographing the spectrum of a standard alloy and comparing the intensities of special lines. It is evident that standard tables of intensities must be available. For further information, consult Smith's *Metallurgical Analysis by the Spectrograph*. The method is particularly suitable for small quantities of impurities in metals. The error involved is of the order of 10 per cent. or less, and is comparable with that of the colorimetric method. The method possesses the great advantage that four or five different elements can be determined almost simultaneously.

Liquids are examined by the absorption method, i.e., a beam of light falls on a glass vessel containing the liquid (e.g., a solution of the sample), and the light passing through is examined by means of the spectroscope. If the conditions are correctly adjusted, the nature of the substance present is indicated by the wavelengths of light which are absorbed, while the amount present is measured in terms of the extent of such absorption. To this end curves are plotted relating the ratio of the intensities of the light of any particular wavelength falling on and emerging from the solution, with the wavelength of the rays used.

For many purposes spectroscopic methods are both sensitive and very accurate, once the necessary technique has been acquired. Thus, in the analysis of certain alloys it has been possible to reduce the working time from four days (for ordinary chemical methods) to three hours.

**The Polarograph.** This is an instrument for carrying out an analysis "automatically." At present it is expensive, but it has been tested by widespread use. The solution to be analysed is placed in a vessel on the bottom of which is a layer of mercury, the anode. The cathode is a stream of fine drops of mercury, falling from a reservoir through the solution. A difference in potential between the electrodes is applied by means of a special potentiometer, which increases this difference automatically as the analysis proceeds. A potential difference-current graph is traced on a drum. Provided the applied potential does not exceed the decomposition potential of any of the salts in solution, there will be no current. When the first decomposition potential is reached, a current proportional to the concentration of the ions in the solution will flow. When the decomposition potential of a second salt is reached, this current will increase, and so on. A stepped curve is thus obtained, the height of the steps on the current axis being proportional to the concentration of the ions. Several elements can be determined simultaneously and rapidly. For example, the copper, zinc and lead in a brass can be found in fifteen minutes, provided the apparatus has been standardised by the use of a similar alloy of known composition.

Not only will the apparatus determine the concentration of metallic ions and of other ionisable and reducible compounds, but it will also determine any substance which can be adsorbed on mercury and reduced. Thus the instrument is of use in metallurgical analysis and in the examination of water, gas, sugar, beer, dye-liquors, etc.

For further information, see Kolthoff and Lingane's *Polarography*.

**Fluorescence Analysis in Ultra-violet Light.** In laboratories where an ultra-violet lamp is available, the application of a number of the analytical methods described in this book may be extended considerably by the methods of fluorescence analysis. This applies particularly to colorimetric and volumetric methods. The principle of the method is the production of fluorescence effects which are usually invisible in ordinary visible light, but which can be seen under an ultra-violet lamp from which visible light is excluded by means of a special filter. The only special apparatus required is the ultra-violet lamp with filter; one of these is now usually to be found in most laboratories.

Since these fluorescence effects can often be produced by extremely small quantities of certain materials, the methods in which they are used have high degrees of both sensitivity and selectivity. As an example, certain substances which become fluorescent or non-fluorescent at a volumetric end-point may be used as indicators; they often enable very dilute solutions to be titrated, and they can function even in solutions which are normally so coloured or turbid that the change in colour of an ordinary indicator is invisible. The use of quinine to indicate end-points involving sulphates (by reason of the vivid fluorescence of quinine sulphate) is an example; the use of dichlorofluorescein as a fluorescent adsorption indicator for halide titrations, and of fluorescein for bromate titrations (p. 182) are others. Colorimetric methods involving the formation of a fluorescent reaction-product have also been developed; a good example of this nature is the determination of aluminium by means of the fluorescence it produces with tetrahydroxy flavanol. The method has numerous applications in qualitative and technical analysis. For further information see Radley and Grant's *Fluorescence Analysis in Ultra-Violet Light*.

# PART V

## APPLIED QUANTITATIVE ANALYSIS

### SECTION X

#### TECHNICAL INORGANIC ANALYSIS

##### The Sampling of Solids

**SAMPLING** is the science of extracting from a large quantity of material a small portion which is truly representative of the whole. Needless to say, sampling and analysis go hand in hand, but it is unfortunately no uncommon experience to find a chemist wasting time and trouble in carrying out a long and careful examination of a material which has been sampled in a slipshod manner.

Only a few of the elementary principles and methods of sampling are described here. It is almost true to say that every material demands special study and must be sampled by special methods, and lack of space forbids approaching a full treatment of the subject. Methods for sampling coal, coke and cement have been laid down by the British Standards Institution in its *Specifications*; and for fertilisers by the Ministry of Agriculture and Fisheries—*Regulations* (1932). Detailed information about other materials must be sought in the special text-books (p. 510). The importance of good sampling cannot be over-estimated. Three facts must always be remembered:

- (a) The larger the sample, the more representative it will be.
- (b) In a mass of ungraded material the composition of the dust will probably be different from that of the lumps.
- (c) In a heterogeneous mass the harder lumps will be different in composition from the softer.

The first operation in the sampling of solids is to obtain the gross sample. The minimum satisfactory weight of this sample depends on the state of division and quality of the material. For example, if the diameter of the largest lump is about 1 inch, it may be that not less than 500 lb. should be taken. If the diameter of the largest lump is 0.13 inch, 4 lb. may suffice; if it is as small as 0.01 inch, 1 ounce may be enough. It is laid down in the case of coals (*B.S. Specification No. 403*) that if the diameter of the largest piece is 3 inches and the ash content of the coal is 20 per cent., at least 650 pounds taken from at least 130 places in the load are required as a representative sample of 50 tons. If the largest piece of a coal containing only 6 per cent. of ash is only 1 inch in diameter, then 40 pounds, taken from twenty places in a load of 50 tons, are required.

The collection of the gross sample is a matter of common sense, and no general rules can be laid down. No serious error will arise if an endeavour is made to take representative samples from units chosen arithmetically, and not because the material looks good or poor or

average; if it is remembered that the more finely-divided portions may be shaken from the rest during transit; that the minimum size of the gross sample to be taken is at least as large as that set out above; and that many increments make up this sample. In the case of coal, it is laid down that the requisite number of increments shall be distributed evenly over the whole number of waggons in the consignment. The increments are taken by scooping narrow holes, at least 1 foot deep, along the lines joining the opposite corners of the waggons and at distances of one-sixth and one-third of the lengths of these diagonals from the corners. The positions of the holes are varied regularly from waggon to waggon.

The next step is to reduce the gross sample. If it is coarse, it is first crushed, usually in a mechanical crusher, to pass an inch-mesh sieve. It is then spread out on a clean, concrete floor and shovelled into a cone. The man must work round and round the layer from the outside to the centre, and every shovelful must hit accurately the top of the cone. Every effort must be made to build a symmetrical pile, because the dust tends to collect in the centre. A good plan is to mount a large funnel over the centre of the cone and to shovel the material through this funnel, which must be raised from time to time, because the material must not fall violently on to the heap, but rather should flow on to it. Sometimes it is advisable to spread out the cone a second time into a layer and to rebuild it as before. (*The Standards Specification* for coal lays down that the cone be built three times.) The spreading is best done by pressing squarely on the top of the cone with a flat board, or if this plan proves impracticable, by shovelling from the centre outwards in a symmetrical manner.

If the cone is built a second time, it must be spread out again. The layer is then halved either by marking it out and shovelling, or by working a board through it and pushing the halves apart. The dividing line must pass accurately through the point above which was formerly the apex of the cone. The halves are quartered by the same methods. The north and south quarters are discarded, care being taken to brush away all the dust, and the *whole* of the material in the other quarters is crushed until the diameter of the largest piece is half that of the largest piece in the first cone.

The crushed material is then coned and quartered exactly as before, the north and south or the east and west quarters being discarded. The residue is again crushed until the diameter of the largest piece has again been reduced by half, and the crushed material is again halved in bulk by coning and quartering; and so on until a sample of suitable weight has been obtained. As soon as its bulk permits, the residue of the gross sample should be placed on a smooth piece of American cloth and mixed by drawing the south corner of the cloth up to and over the north corner in such a way that the sample does not slide, but rolls, over and over itself. Then the north-west side of the cloth may be drawn up to and over the south-east side, and so on until the sample is thoroughly mixed. The heap is then rolled to the centre of the cloth, spread out and quartered as before. A scoop such as is used by a teller in a bank is most useful for handling the quarters when they have been sufficiently reduced in size and bulk. When a small representative sample has been obtained, it

must be crushed in a hand-mill or ground in an agate or other mortar until the *whole of it* passes through a sieve of the chosen mesh. As the harder material will probably be the last to pass through the sieve and will therefore be found on the top of the heap, the whole of the material must be mixed thoroughly on oil-cloth or paper before it is bottled or analysed.

During the operations of crushing and sampling the material will probably have become heated and may have lost moisture. It can be dried at some standard temperature, perhaps at  $105^{\circ}\text{C}$ ., or it may be spread out in a thin layer and left exposed to the atmosphere, but out of sunlight, until it has come into equilibrium with the water vapour in the air by gaining or losing moisture. If the second method is used, notes should be made of the temperature and humidity of the air in the room. It is most important that a careful note of the history of the material after sampling should be made. *E.g.*, "Through 85-sieve. Bottled at once after sampling," or "Through 85-sieve. Air-dried. Room temperature  $16^{\circ}\text{C}$ . Normal atmosphere." The principal object of air-drying is to bring the material to such a state that its composition will not change to an important extent while it is being transferred from one vessel to another, or when it is being weighed out during the ordinary course of analysis. If there is danger of the moisture content of the gross sample changing during crushing and sampling, a large portion of the gross sample, perhaps 10 pounds in weight, should be taken off either at once or when the material has been reduced to lumps of approximately 1 inch in diameter. The whole of this sample should either be completely dried under the standard conditions, or should be air-dried and the loss of weight noted.

That portion of the sample which is not required for immediate use must be kept in an air-tight bottle.

The sampling of metals and alloys is an even more difficult problem. The point to remember is that those constituents of an alloy which melt at the lowest temperature are usually to be found near the centre of an ingot or casting. As a general rule, these low-melting constituents will be the impurities, and therefore the material at the centre of such an ingot will be of poorer quality than the average. Occasionally, also, there is a band of material which is not representative of the whole near the outside of an ingot.

Segregation in certain metals and alloys is negligible, and in such cases it matters little how the sample is taken. In other cases, turnings from the outside of a rod may give material much poorer or somewhat richer than the average. For this reason it is better to sample by drilling rather than by turning. To sample a bar, it is usual to drill holes, preferably right through the metal, about half-way between the centre and the outside on both sides of the central plane.

Sometimes an alloy contains two constituents. One of these may be soft and ductile, the other hard and brittle. In this case it is important to make sure that *all* the material from any one hole is analysed, because any fine dust will be of different composition from the more ductile drillings. Grey cast-iron, for example, is a mixture of comparatively soft and ductile iron and easily-powdered graphite. If fine drillings are taken from a casting and are analysed without the dust, they will be found to contain considerably less carbon than coarse drillings.

If the alloy, e.g., Devarda's alloy, is brittle, it is best to crush a fairly large piece in a percussion mortar (p. 23), and to sieve and mix it as an ore should be sieved and mixed.

If the sample of a metal or alloy has been contaminated with oil, it can be cleaned by washing it first with ether and then with alcohol or acetone, and by heating it in a steam-chamber. The drillings, which are often surprisingly difficult to dry, should not be heaped up, but should be spread out in a thin layer in the chamber.

When a sample of a metal is being taken, there is a chance of fragments of steel being torn off from the tools or mortar used, and these fragments will enter the sample. If the metal or alloy is non-magnetic, these can be removed by passing the material between the poles of a fairly powerful electro-magnet or even by rubbing an ordinary magnet lightly over the drillings.

### Determination of Silver and Copper in a Copper-Silver Alloy

Most samples of silver plate contain about 925 parts of silver per thousand. The remainder may be any metal, but is usually copper. Volumetric and gravimetric methods for the analysis of a copper-silver alloy of this type are described below.

*Volumetric Determination of Silver.* Weigh out a piece of the alloy of about 0.3 gm. weight, and dissolve it in 10 ml. of 50 per cent. nitric acid in a bottle made of resistance glass and provided with a stopper. Remove nitrous fumes by boiling on a hotplate without the stopper. Cool. Dilute to about 100 ml., add 2 drops of phenosafranine, and titrate with an arbitrary solution of sodium chloride containing approximately 6 gm. of the salt per litre (p. 191); or titrate with approximately decinormal potassium thiocyanate, using a ferric salt as indicator (p. 197).

In either case, the solution used must be standardised against a known weight of about 0.25 gm. of pure silver, to which about 0.02 gm. of copper has been added. This mixture should be dissolved and titrated in exactly the same way as for the sample. Reliance must not be placed on a single titration. Much time will be saved if three solutions each of the alloy and standard are prepared simultaneously.

*Volumetric Determination of Copper.* Dissolve 1 gm. of the alloy in a small excess of nitric acid, using a covered beaker. Remove the nitrous fumes by boiling, dilute to about 100 ml., and again heat the solution to boiling. Run in, slowly and with constant stirring, sodium chloride solution in slight excess. When the precipitate has settled, filter the solution and wash the precipitate with hot water to which a few drops of nitric acid have been added. Collect the filtrate in a large evaporating-dish and evaporate the liquid nearly to dryness on a hotplate. Transfer the solution to a conical flask, using as little water as possible for washing the dish. Neutralise the solution with sodium carbonate solution, clear any precipitate with dilute acetic acid, and determine the weight of copper present by the iodide method (p. 177). Titrate with 0.05 N. sodium thiosulphate.

*Gravimetric Determination of Silver.* Dissolve and precipitate the silver in 0.5 gm. of the alloy as described above under "Copper," and then proceed as directed on p. 74.

*Gravimetric Determination of Copper.* Collect the filtrate and washings from the gravimetric determination of the silver in an evaporating-dish. Add 10 ml. of dilute sulphuric acid and evaporate to white fumes. To ensure that all nitric acid has been removed, wash down the cold dish with a little water, and again evaporate to fumes. Cool, dissolve any precipitate in water, and determine the copper by the thiocyanate method (p. 61).

Note that the weight of cuprous thiocyanate obtained will probably be very small. The alternative is to start with 5 gm. of alloy, but the determination will then be laborious, because of the considerable amount of silver chloride which must be handled. This is one of the many instances where a volumetric method is preferable to a gravimetric method.

### Indirect Determination of Arsenic in Ores by Thiocyanate

The arsenic is converted into alkaline arsenate by fusion with alkaline carbonate and nitrate: the melt is extracted with water and the arsenate is precipitated as silver arsenate by the addition of an excess of a solution of silver nitrate. The silver in the silver arsenate is determined by the thiocyanate process (p. 197). It is evident that the ore must contain no phosphorus, since this would be determined as arsenic.

From 0.1 to 1.0 gm. of the finely-powdered ore is fused in a nickel crucible with ten times its weight of a mixture in equal proportions of  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ . A layer of the alkali salts must cover the mixture. The cold mass is extracted with boiling water, and the insoluble matter is filtered off. The filtrate is acidified with dilute nitric acid and is boiled to expel carbon dioxide and oxides of nitrogen. The solution is made just alkaline by the addition of ammonia, and is boiled again and filtered from any slight precipitate which may have been produced.

A solution of silver nitrate is added in quantity more than sufficient to precipitate the arsenate, and the precipitate is dissolved by adding 50 per cent. nitric acid a drop at a time. The silver arsenate is reprecipitated in a compact form by adding 10 ml. of a saturated solution of sodium acetate and by heating just to boiling. The silver arsenate is allowed to settle, and it is filtered off when cold and collected in a Gooch crucible. The precipitate is washed with cold water until the filtrate contains no silver, and it is then dissolved in a small volume of 50 per cent. nitric acid. The crucible is washed thoroughly with water, and the solution is diluted to about 100 ml. Two millilitres of the ferric sulphate solution (p. 197) are added, and the silver is titrated with the standard thiocyanate solution.

### Evaluation of Chrome Iron Ore

For the evaluation of ordinary iron ore, see p. 187.

The value of this mineral for commercial purposes depends almost entirely on the proportion of chromium which it contains: the percentage of chromic oxide ( $\text{Cr}_2\text{O}_3$ ) should not fall below 40, if the ore is to be of commercial value.

The chromium may be determined by fusing the ore with sodium peroxide. Subsequent treatment with boiling water and filtration from the insoluble oxide of iron gives a solution of  $\text{Na}_2\text{CrO}_3$ , which may be converted into  $\text{Na}_2\text{Cr}_2\text{O}_7$  by the addition of  $\text{H}_2\text{SO}_4$  in excess. The acidified solution may now either be titrated with standard ferrous sulphate solution, either electrometrically or with an internal or external indicator; or an excess of ferrous sulphate can be added and the ferric iron produced determined with  $\text{TiCl}_3$ ; or excess of  $\text{KI}$  solution may be added and the free iodine titrated by standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution, using starch as indicator.

**Conversion of the Chromium into Sodium Dichromate.** Mix about 0.5 gm. of the ore, which must be in the form of an impalpable powder, with ten times its weight of dry sodium peroxide in a thick-walled porcelain crucible, of about 50 ml. capacity. Cover the mixture with a further 2 gm. of sodium peroxide, and heat the crucible and its contents to about  $700^\circ \text{C}$ . in a muffle furnace. When the material has melted and is resting quietly in the crucible, keep it molten for a further five minutes, and stir it twice or thrice with a stout platinum wire. If a furnace is not available, place the crucible on a triangle and heat it with a Bunsen burner, which must be held in the hand and moved about.

Place the cold crucible in a large beaker, add about 200 ml. of water, and heat until the yellow mass has completely disintegrated. At this stage, remove the crucible and allow the solution to cool. Add 1 to 2 gm. of sodium peroxide, and boil the solution thoroughly to decompose the hydrogen peroxide, and any manganate or ferrate which may have been formed during the fusion. Then add about 10 gm. of solid ammonium carbonate and boil for five minutes longer to reduce the concentration of sodium hydroxide: otherwise during the subsequent filtration, the filter-paper may be attacked. Free sodium hydroxide must, however, still be present in the solution. Filter the liquid when it has become cold, wash the residue thoroughly with hot water, and make up the filtrate and washings to 500 ml.

Acidify an aliquot portion with dilute sulphuric acid, and titrate with 0.05 N. ferrous ammonium sulphate, using ferrous phenanthroline as indicator (p. 145); or determine the dichromate by any of the other methods mentioned above.

*Note.* As chrome iron ore is not readily attacked even by sodium peroxide, it is advisable to treat the residue on the filter-paper with hot, dilute sulphuric acid. Any coloured, insoluble matter will probably contain chromium, and must be dried and ignited in the paper, and fused once more with sodium peroxide.

For the Composition of a Typical Sample of Chrome Iron Ore, see Table III., p. 491.

### Evaluation of Mercury Ore

In determining the percentage of mercury in a good sample of cinnabar (native mercuric sulphide), or other rich mercury ore, the material should be heated with lime and the mercury collected in water (p. 98). Poor ores should be decomposed by heating them with iron. The mercury is condensed on a weighed sheet of silver, with which metal it forms an amalgam, and the weight of mercury is obtained on reweighing the sheet. The process is described below in detail.



The Apparatus required is shown in Fig. 104, and is prepared as follows: The upper edge of a glazed porcelain crucible (*a*), about 4.5 cm. in height

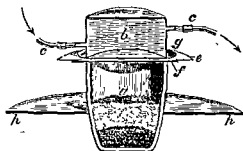


FIG. 104. EVALUATION OF CINNABAR.

and 4 cm. in diameter, is ground down flat on a rough surface. A 5-cm. disc, or square of "fine" silver sheet (*f*), weighing about 0.3 gm. per square centimetre, is annealed in a flame, and is rubbed between smooth surfaces until it lies perfectly flat upon the top of the crucible. Upon this is placed a somewhat larger sheet of thin silver foil (*e*) to keep the sheet (*f*) clean. A copper cooler (*b*), through which cold water constantly passes through two tubes (*c*), is laid upon the silver foil (*e*) and is pressed down by placing a weight upon it. A metal gutter (*g*) should run round the cooler to collect any condensed moisture, which may be removed from time to time by blotting-paper. The crucible is supported in a suitable hole cut in a metal or asbestos sheet (*h*).

The iron filings, which are to be mixed with the ore, are cleaned by heating them to redness in a covered crucible for an hour and by sifting them, when cold, through a 100-mesh sieve: another batch of filings for placing above the mixture in the crucible may be sifted through a 40-mesh sieve, and kept separate.

**Procedure.** The finely-powdered ore is dried necessary, preferably over  $\text{H}_2\text{SO}_4$  in a desiccator, as free mercury may otherwise be partially removed as vapour. The ore is introduced into the crucible (*a*). About 2 gm. should be taken if the percentage of mercury present is less than 1 per cent.; 1 gm. if the percentage is between 1 and 2; and 0.5 gm. or less if the percentage is between 2 and 5. If the ore contains more than 5 per cent. of mercury, it should be ground until it *all* passes a B.S. 150-sieve, and mixed intimately with a suitable, known weight of sand or calcite which has been ground to pass the same sieve.

The ore is mixed in the crucible with about 10 gm. of the finer iron filings, and the mixture is covered with about 5 gm. of the coarser filings. The crucible is covered by the silver plate, and the other fittings are put in place. A flame just large enough to heat the bottom of the crucible to redness, and which does not come into contact with the sides, is applied. After twenty minutes, the flame is removed, and, as soon as the whole is cool, the silver plate is taken off, dried for one or two minutes in a steam-oven, and weighed when cold (*Note*). If any tarry matter has collected on the plate, this must be removed by treatment with alcohol before the plate is dried. The increase in the weight of the silver plate gives the weight of mercury in the portion of ore taken.

**Note.** Unless some experience has been obtained in the adjustment of the size of the flame and the length of time required for the heating, it is well to reheat the residue in the crucible with a fresh silver plate in order to make sure that the whole of the mercury has been collected.

It is possible to judge whether the plate was absolutely flat on the top of the crucible by noting whether the mercury stain upon it is perfectly circular and of the same area as that of the top of the crucible. The close-fitting of the plate is essential to ensure against loss of mercury vapour.

The silver plate may be prepared for another determination by heating it gently to volatilise the mercury.

### Evaluation of Zinc Ores

Zinc is nearly always determined volumetrically by the ferrocyanide method (p. 199). As many elements, notable lead, copper, cadmium, iron and manganese, interfere, the principal difficulty is the preparation of a solution of the ore free from these metals. A preliminary qualitative analysis of the ore should always be made to find out whether the absence of certain elements enables the scheme for separation to be simplified.

*Quantities.* Suppose the ore contains about 40 per cent. of zinc. It has been shown (p. 200) that a solution containing 10 grm. of zinc (or 25 grm. of ore) per litre will be approximately equivalent to a ferrocyanide solution containing 45 grm. of the salt crystals per litre. As the separation may involve the use of considerable volumes of liquid, let us decide to prepare 500 ml. of the ore solution and to titrate portions of 50 ml. at a time. We therefore should take 6 grm. (say) of the ore, but as this is too much to handle conveniently, take 3 grm. and use a ferrocyanide solution containing 2.25 grm. per litre.

*Method.* Place a suitable weight of the ore in a large porcelain basin covered with a filter-funnel, and dissolve it in hydrochloric acid, with the addition, from time to time, of a few drops of nitric acid. When solution appears to be complete, clean and remove the funnel, and add 5 ml. of concentrated sulphuric acid. Evaporate until dense white fumes appear. Extract the residue, which will contain any silica or lead originally present in the ore, with water, and filter. Collect the filtrate and washings in a beaker.

Bring the volume of the solution to 100 to 150 ml. and add 2 ml. of concentrated hydrochloric acid. Heat nearly to boiling and saturate with  $H_2S$ , as far as possible keeping the beaker covered with a clock-glass. Keep on passing the  $H_2S$  slowly until the solution is nearly cold, but towards the end pass the  $H_2S$  rapidly again. Filter through paper, and wash with water saturated with  $H_2S$  and containing about 50 ml. of concentrated sulphuric acid per litre, until the filtrate fails to show a chloride reaction with a solution of silver nitrate. To test for chloride, add silver nitrate in excess to the filtrate, make alkaline with ammonia, filter, and acidify the filtrate with nitric acid. A white precipitate or opalescence shows the presence of chloride. Copper and cadmium should now have been removed as sulphides.

*Note 1.* Cadmium may be difficult to separate. Before filtering, decant a small volume of the clear solution, add twice its volume of water, and pass  $H_2S$ . No further precipitate should form. Return this test-portion to the original solution, and, if necessary, owing to the presence of cadmium in the liquid, dilute, heat to  $70^\circ$  to  $80^\circ$  C., and pass in  $H_2S$  again while the solution is cooling.

*Note 2.* It is almost impossible to separate zinc completely from copper and cadmium by the  $H_2S$  method. If the  $P.H.$  of the solution is too low, some down. If it is large, to oxide, redissolved and reprecipitated, the two filtrates being combined.

rate the

To remove iron and manganese, boil the filtrate from the sulphides to remove the  $\text{H}_2\text{S}$ , and add a few millilitres of concentrated nitric acid to oxidise the iron. Cool the solution, and add bromine and then ammonium hydroxide in slight excess. Boil, and filter off the precipitate of hydroxides, washing them with water containing 5 gm. of ammonium chloride per 100 ml. This precipitate will contain some zinc. It should therefore be dissolved in a small volume of hot, 50 per cent. hydrochloric acid and be reprecipitated, the two filtrates being combined. Make up the filtrate to 500 ml. in a measuring-flask and determine the zinc in a 50-ml. portion by the ferrocyanide process (p. 109).

### Evaluation of Copper Ores

Four useful methods for the determination of copper are available.

**The Electrolytic Method.** Weigh accurately about 2 gm. of the finely-powdered sample, or less if the ore is rich in copper. If it contains bituminous matter, or sulphur, roast the powder in the air. Treat the residue with 15 ml. of concentrated nitric acid, in an evaporating-dish, and evaporate nearly to dryness. Cool. Add 5 ml. of concentrated hydrochloric acid, and make sure that all solid matter in the dish is wetted with this acid. Add 5 ml. of concentrated sulphuric acid and remove all chlorine by evaporating down to dense white fumes. Dissolve the copper sulphate in water, adding a few drops of nitric acid if necessary, and filter off the residue. Collect the filtrate and washings in a 150-ml. beaker of a shape suitable for the electrodeposition (p. 226). Add ammonia until the blue colour of the cuprammonium ion is seen, or until there is a slight, permanent precipitate. Add nitric acid, and electrolyse as described on p. 228.

The residue on the filter-paper should be tested to ensure that it contains no copper. Electrodeposition is unsuitable when much iron is present. Iron should be removed (*e.g.*, as in the cyanide process), or another method should be chosen.

**The Cyanide Method.** The ore is dissolved in acid, and the whole of the copper is precipitated by immersing aluminium sheet in the solution. The copper is separated and dissolved in nitric acid. This solution is titrated with a solution of potassium cyanide, after it has been made alkaline by the addition of sodium carbonate and ammonium hydroxide.

Take about 0.5 gm. of the finely-powdered ore and treat it in succession with nitric, hydrochloric and sulphuric acids as described above. Only about 5 ml. of nitric acid need be used. When dense white fumes of sulphuric acid have been produced, cool, add 25 ml. of water, and reheat to dissolve any ferric sulphate. Filter, and collect the filtrate in a small beaker. Keep the volume of filtrate and washings smaller than 75 ml. Introduce two pieces of aluminium sheet, each about 40 mm. square and 1.5 mm. thick, and with their corners bent over in such a way that they cannot lie flat against each other or against the bottom of the beaker. Cover the beaker, and boil the contents gently for ten minutes.

Add 15 ml. of a saturated solution of  $\text{H}_2\text{S}$ -water to precipitate the last traces of copper, and separate the aluminium, either by pulling out the sheets and placing them in a second beaker, or by pouring the solution,

with as much of the copper precipitate as possible, into a second beaker. Decant the liquid from the copper through a paper, keeping as much of the copper as possible in the beaker. Wash the copper three times with about 20 ml. of  $H_2S$ -water each time, passing the liquid through the paper. Discard the filtrates.

Add 5 ml. of 50 per cent. nitric acid to the beaker containing the aluminium, and warm gently. Any copper adhering to the sheets or to the glass will be dissolved. Pour this solution slowly through the paper, and collect the filtrate in the beaker containing the copper precipitate. Wash the paper with 5 ml. of bromine water, or with sufficient bromine water to colour the filtrate, and then with hot water, and also wash the beaker with hot water. Remove the excess of bromine by boiling the solution.

Make the solution just alkaline by adding a solution of sodium carbonate, and then add 1 ml. of dilute ammonium hydroxide. Titrate with a solution containing about 40 gm. of potassium cyanide per litre, until the copper solution is just decolorised. Standardise the cyanide against a solution made by dissolving about 0.2 gm. of pure copper foil in 5 ml. of nitric acid, removing nitrous fumes by boiling, diluting to about the same volume as that of the ore solution, and treating with sodium carbonate and ammonia as before. See also p. 197.

*Note.* A small quantity of ferric hydroxide may be in suspension in the alkaline solution of the copper from the ore. Its presence will be due to an imperfect separation, and it will make the judgment of the end-point more difficult. Its effect may be counteracted by the addition of ferric sulphate in approximately equivalent quantity to the standard solution of copper, before the sodium carbonate and ammonia are added.

**The Iodide Method.** Prepare a solution of the copper by treatment with acid, separation with aluminium, and dissolution in nitric acid and bromine water as described above under "Cyanide Method." The portion of ore taken should contain about 0.15 gm. of copper.

Add sodium carbonate solution to the solution of copper until a small, permanent precipitate is formed, and then dissolve this precipitate in a very small excess of acetic acid. Add potassium iodide, and determine the liberated iodine with approximately decinormal sodium thiosulphate (p. 177). If iron is present, add 2 gm. of  $KHF_2$  before the iodide is added, to prevent the ferric iron reacting to produce iodine. A complex, unionised compound of iron and fluorine is formed.

**Cuprous Thiocyanate Method.** Treat the ore in succession with nitric acid, hydrochloric acid and concentrated sulphuric acid as is described under "Electrolytic Method." Evaporate to dense white fumes. All nitric acid must be removed. Cool, add 25 ml. of water, reheat, and filter.

Precipitate the copper as cuprous thiocyanate and weigh it as such (p. 61); or determine the thiocyanate volumetrically by the iodate process (p. 181); or dissolve it in nitric acid, fume the solution with sulphuric acid and determine the copper electrolytically.

*Note.* Under the above conditions, of the common metals only copper, lead and mercury are precipitated as thiocyanates. Mercury is rarely present in a copper ore; the lead, in this case, will have been removed as lead sulphate.

Precipitation as thiocyanate is a convenient and clean method of separating copper from cadmium, tin, zinc, nickel, iron, etc.

For the Composition of a Sample of Copper Pyrites, see Table IV., p. 492.

### Evaluation of Cassiterite

This mineral consists mainly of  $\text{SnO}_2$ , and its commercial value depends largely on the percentage of tin which it contains. The ore is "broken up" by fusion with sodium hydroxide, and the sodium stannate is extracted with water. The solution is strongly acidified, and the tin, after reduction with nickel foil or powdered antimony, is oxidised with iodine or potassium bromate.

Weight out accurately about 1 gram. of the very finely powdered ore. Fuse about 10 gram. of stick sodium hydroxide in an iron crucible of about 50 ml. capacity. When the molten sodium hydroxide is quiet, cautiously add the weighed sample to it, and heat cautiously. Ultimately heat with the full flame of a Bunsen burner until the liquid in the crucible is quiet. Cool, and extract the melt with hot water. Make up the solution, without filtering, to 250 ml., and transfer a suitable volume of it to a reduction-flask (p. 166); or, if the ore is poor, transfer all the liquid to the flask. About 0.15 gram. of tin is a suitable quantity to reduce.

Dilute the aliquot portion to about 200 ml. Neutralise it with hydrochloric acid, and add hydrochloric acid in excess to bring the content of free acid to between 25 to 50 per cent. by volume. Reduce the tin in an atmosphere of  $\text{CO}_2$ , either with nickel foil or with about 1 gram. of precipitated antimony (p. 166). Cool the reduced solution, while maintaining the atmosphere of  $\text{CO}_2$ , and then titrate it with a decinormal solution of iodine, using starch as indicator; or add to it a small crystal of potassium iodide together with starch, run in a decinormal solution of potassium bromate rapidly from a burette, using a small excess of the bromate, and titrate this excess with a standard solution of sodium thiosulphate.

*Note.* Only tungsten, of the elements usually present in tin ores, will interfere with this evaluation. Tungsten is reduced to the blue, quinquevalent form, but is not reoxidised by iodine. The intense blue colour may, however, mask the

the residue on the leaving any tin 1 few millilitres of filtrate, which can has been adjusted suitably.

### Evaluation of Soda Ash

Soda ash is essentially sodium carbonate, but it may contain hydroxides or bicarbonates, chlorides, sulphides, sulphites, sulphates, and water, together with other substances, as impurities.

To prepare a solution for analysis, dissolve 10 gram. of the sample in boiled, distilled water. Filter, but only if there is a considerable quantity of undissolved matter, and dilute the filtrate to 1 litre.

**Total Alkali.** Titrate 50 ml. of the solution with standard sulphuric or nitric acid of approximately decinormal concentration, using methyl orange as indicator. The use of nitric acid is advantageous in connection with the determination of chlorides. The result of the titration gives a measure of the total carbonate, bicarbonate or hydroxide, and sulphide.

**Sodium Carbonate and Other Alkali.** Titrate a second 50-ml. portion of the solution of the standard acid, using phenolphthalein as indicator. If the volume of acid used with methyl orange is substantially more than double that now used, the soda ash contains bicarbonate; if less than double, the ash contains hydroxide. In the former case, add a suitable quantity of standard sodium hydroxide to an aliquot portion of the sample-solution, and determine the bicarbonate by the method given on p. 180. In the latter case, precipitate the carbonate with barium chloride and titrate the hydroxide with standard acid (p. 129). In doubtful cases, add sodium hydroxide before precipitating the carbonate.

If an appreciable quantity of sodium sulphide is present in the ash, cool the vessel containing the barium carbonate and sodium hydroxide. Filter, and titrate the filtrate with acid, using methyl orange as indicator. The result gives sodium hydroxide (or bicarbonate) and sulphide.

**Sulphide plus Sulphite.** Neutralise an aliquot portion of the original solution with acetic acid, and then add that acid in slight excess. Titrate with 0.1 N. iodine, using starch as indicator. The volume of iodine used gives sulphide and sulphite (pp. 169 and 170).

**Sulphide.** First test to find out whether sulphide is present. Use sodium nitroprusside paper, which is turned purple by sulphides in alkaline solution.

If sulphide is found, add a few millilitres of ammonia to 100 ml. of the original solution, and titrate the boiling liquid with an ammoniacal solution of silver nitrate containing approximately 10 grm. of silver per litre, until a precipitate of silver sulphide ceases to be formed. If much sulphide is present, the precipitate must be removed by filtration just before the end-point is reached, and the titration must be completed by adding the necessary few drops of the silver solution to the hot filtrate; or an excess of silver solution may be added, and the silver sulphide collected and weighed.

The percentages of sodium hydroxide, sodium sulphide and sodium sulphite in the ash can now be calculated.

**Chloride.** Neutralise 100 ml. of the original solution with nitric acid, adding a few drops of the acid in excess. If nitric acid has been used in the determination of total alkali, the volume required will already be known. Remove the  $H_2S$  by boiling the solution. Neutralise the small excess of nitric acid with a small quantity of precipitated chalk, and titrate the chloride with a decinormal solution of silver nitrate, using potassium chromate as indicator (p. 193).

**Sulphate.** Acidify a suitable volume of the solution with hydrochloric acid, filter if necessary, and determine the sulphate gravimetrically as barium sulphate (p. 65).

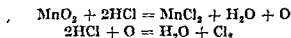
**Loss on Ignition.** Ignite 10 grm. of the sample in a platinum crucible at 300° C. for half an hour. The loss in weight is due chiefly to moisture and to organic matter. If an exact analysis is required, a smaller quantity must be heated in a tube and the water collected and weighed (p. 92). Allowance must be made for the water and carbon dioxide of constitution of any sodium bicarbonate present. These will also be driven off at 300° C.

**Insoluble Matter.** Dissolve 20 grm. of the sample in 200 ml. of warm water. Allow any residue to settle. Filter through a weighed filter-paper. Wash thoroughly until the filtrate no longer shows an alkaline reaction, and dry at 105° C.

Similar methods are used for black ash.

### Evaluation of Manganese Ores

The value of a manganese ore for the preparation of chlorine and for many other purposes depends upon the amount of "available oxygen" which it contains, namely, that part of the oxygen which is available for oxidation when the ore is treated with an acid.



Thus, half the oxygen in pure manganese dioxide is "available."

Three methods for determining the oxidising value of a manganese ore are described below. Many samples contain ferrous oxide. This reduces the actual amount of "available" oxygen in the ore, because a portion is spent uselessly in converting the iron to the ferric state. The amount of oxygen actually available in practice can be determined by either method (a) or (b). A more accurate determination of the manganese dioxide in the sample can be made by method (c). The determination of the *total* manganese in the ore is described on p. 267.

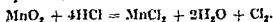
About 10 grm. of the oxide are powdered as rapidly and as finely as possible, and the powder is placed in a stoppered weighing-bottle.

**Moisture.** Most manganese ores contain combined water, in addition to hygroscopic moisture. To determine the hygroscopic moisture weigh out from 2 to 4 grm. of the ore accurately in a pair of watch-glasses, and heat the sample in an air-oven at 120° C. until its weight becomes constant. Alternatively, heat 2 grm. of the ore in an electrically-heated tube at 120° C. and collect the water evolved. Only the moisture absorbed hygroscopically by the ore is driven off at this temperature.

#### Available Oxygen (a) by Potassium Iodide and Thiosulphate.

About 0.5 grm. of the finely-powdered ore is accurately weighed into the small flask (Fig. 83, p. 175), and is warmed with about 25 ml. of concentrated hydrochloric acid; the chlorine which is given off is absorbed in potassium iodide solution contained in the U-tubes. The chlorine liberates its chemically-equivalent quantity of iodine, and this is then titrated with standard sodium thiosulphate solution (p. 175).

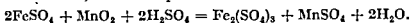
The available oxygen is usually calculated in terms of manganese dioxide, according to the equation,



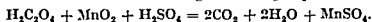
**Available Oxygen (b) by the Oxidation of a Ferrous Salt.**

Digest about 1 gram. of the accurately-weighed and finely-powdered ore with dilute sulphuric acid and 100 ml. of a solution of ferrous sulphate containing about 120 gram. of the crystals per litre, in a flask fitted with a Bunsen valve. Cool, and make up the solution to 500 ml. Titrate an aliquot portion with  $\text{TiCl}_3$  solution of approximately decinormal concentration, using thiocyanate as indicator. A correction of the results for any ferric iron present in the ferrous solution must be made, and the  $\text{TiCl}_3$  must be standardised against a standard ferric solution at the time of the experiment (p. 187). Alternatively, a known weight of the ferrous salt may be digested with the ore as above, and the excess of this salt determined with standard dichromate.

The available oxygen is usually calculated from this result, in terms of manganese dioxide, from the equation.

**Available Oxygen (c) by the Oxidation of Oxalic Acid.**

Reference to p. 156 will indicate another method of evaluating a manganese ore, which may be applied gravimetrically or volumetrically. The volumetric process is the faster and the more accurate. The weight of oxalic acid which can be oxidised by the manganese dioxide is obtained by this method; 90 gram. of  $\text{H}_2\text{C}_2\text{O}_4$  correspond with 87 gram. of manganese dioxide, and from this relation the weight of  $\text{MnO}_2$  may be calculated.



**Gravimetric Method.** Weigh out accurately about 3 gram. of the finely-powdered manganese ore (*Note*, p. 91). Introduce this, together with two and a half times its weight of neutral potassium oxalate, into a decomposition-flask (p. 86), allow dilute sulphuric acid to flow in, and collect and weigh the  $\text{CO}_2$  which is evolved (p. 87).

**Volumetric Method.** Pour upon 1.5 gram. of the powdered ore, contained in a flask, 50 ml. of normal oxalic acid solution and 3 or 4 ml. of concentrated sulphuric acid. Heat the mixture until all black grains have disappeared. The ore must originally be in a very fine state of division. Filter the liquid, make up the filtrate to 250 ml., and determine the amount of undecomposed oxalic acid in this solution by titrating it with decinormal permanganate solution. The weight of oxalic acid which has been oxidised by the  $\text{MnO}_2$  is then found by difference.

**Determination of Manganese in Manganese Ores**

**The Bismuthate Method.** A rapid and accurate method of determining the total manganese in an ore consists in converting the manganese into permanganic acid by sodium bismuthate, and using this permanganic acid to oxidise a known weight of a ferrous salt. The ferrous salt is present in excess, this excess being back-titrated with standard potassium permanganate.

Take 2 gram. of the finely-powdered ore and digest them with 30 ml. of concentrated hydrochloric acid in a basin covered by an inverted funnel. Any residue should be white. When solution is complete, clean and remove the funnel, add 10 ml. of concentrated sulphuric acid, and evaporate down



to white fumes. Cool, wash down the sides of the dish with a little water, add 10 ml. of dilute sulphuric acid, and repeat the evaporation to white fumes. All chlorine must be expelled. Cool, filter, and make up the solution to 500 ml.

To 25 ml. of this solution, or such portion of it as will probably contain about 0.03 gram. of manganese, add 20 ml. of concentrated nitric acid, and dilute to 100 ml. The concentration of nitric acid must preferably be between 15 to 20 per cent. by weight. Add 1 gram. of sodium bismuthate to the solution, which should have been cooled to 10° C. Shake the contents of the flask, and leave the flask in an inclined position for five minutes to allow the solid matter to settle. The bismuthate will oxidise the manganese salt to permanganic acid.

Filter the solution through a Gooch crucible into a large filter-bottle taking care that none of the pink liquid is drawn into the side-tube and lost. Wash the solid in the flask by decantation with a solution containing 20 ml. of concentrated nitric acid per litre, until the filtrate is no longer pink. This nitric acid must be free from nitrous acid. Very little of the solid in the flask should find its way into the crucible. If the manipulation is well done, the crucible can be used again and again for filtering successive solutions.

Dilute the liquid in the filter-bottle until the nitric acid content is below 3 per cent. The bottle may now be cooled in ice, though this is not absolutely necessary. Add a measured excess, say, 50 ml., of a solution of ferrous ammonium sulphate containing about 40 gram. of the crystals per litre, and titrate at once with standard potassium permanganate of approximately decinormal concentration.

Standardise the ferrous solution by adding 25 ml. of that solution to the spent and titrated liquid in the bottle, and titrate with the permanganate. Under these conditions, the nitric acid oxidises the ferrous sulphate only slowly, and very accurate results are obtainable.

The following is a record of experimental results :

Weight of ore taken = 2.032 gram.

This was dissolved to make 500 ml. of solution.

Concentration of  $\text{KMnO}_4$  = 3.13 gram. per litre.

*Reducing Agents.*

*Oxidising Agents.*

50 ml.  $\text{FeSO}_4 \equiv$  25 ml. of ore solution + 16.7 ml.  $\text{KMnO}_4$

25 ml.  $\text{FeSO}_4 \equiv$  30.6 ml.  $\text{KMnO}_4$

Therefore 50 ml.  $\text{FeSO}_4 \equiv$  61.2 ml.  $\text{KMnO}_4$

Hence in 25 ml. of ore solution is as much manganese as is in

$$(61.2 - 16.7) = 44.5 \text{ ml. of } \text{KMnO}_4.$$

This quantity is

$$\frac{44.5 \times 3.13 \times 55.0}{158 \times 1000} = 0.0485 \text{ gram. of manganese.}$$

This weight is present in  $\frac{2.032}{20}$  gram. of ore.

Therefore the percentage of manganese in the ore is

$$\frac{0.0485 \times 100 \times 20}{2.032} = 47.7.$$

### Analysis of Limestone, Dolomite and Lime

Limestone consists essentially of varying proportions of calcium and magnesium carbonates. If the proportion of magnesium carbonate is

large, the limestone is called magnesian limestone or dolomite. Limestone also usually contains moisture, silicious matter, iron, and aluminium; and occasionally manganese, alkali metals, and organic material. Since the constituents of limestone may vary, an exhaustive qualitative examination should precede the quantitative analysis.

A quantitative analysis of lime may be made by the scheme now suggested for limestone: moisture removable in the air-oven will usually be absent, and little or no carbon dioxide will be found if the lime has been thoroughly and recently burnt. The evaluation of lime and limestone for agricultural purposes is described on p. 332.

For practice in the following scheme of quantitative analysis, select a homogeneous piece of dolomite. Reduce about 10 gm. of the substance to a fine powder, and place the powder at once in a stoppered weighing-bottle.

**Moisture.** Dolomite rarely contains much moisture. If it is necessary to ascertain the percentage of moisture present, the powder should be dried at 200° C. to constant weight.

**Carbon Dioxide.** Decompose the carbonate with hydrochloric acid, and determine the carbon dioxide which is evolved as is described on p. 86, using the apparatus shown in Fig. 62.

Use two soda-lime absorption-tubes (*f*, p. 86). The second tube, or "guard tube," ensures complete absorption of the carbon dioxide. It also indicates when the soda-lime in the first tube must be replaced, because the second absorption-tube undergoes a marked increase in weight once the soda-lime in the first tube is nearly spent.

**Silicious Matter.** The insoluble residue which is left in the flask consists mainly of sand and clay. A small quantity of silica will probably also have passed into the acid solution. The whole of the silica which was originally present in the limestone may be determined as follows:

Transfer the contents of the decomposition-flask after the determination of carbon dioxide to a porcelain dish 10 cm. in diameter, add 10 ml. of concentrated hydrochloric acid, and evaporate the liquid to dryness on a water-bath. Heat the dish in an air-bath at 110° C. for an hour, in order to convert the silica into the anhydrous, insoluble condition.

Allow the dish to cool, and then gently warm its contents with 20 ml. of concentrated hydrochloric acid, which will dissolve everything except the silica and the clay. Dilute with water, filter, and wash the residue in the filter until it is free from acid. If the residue is large, again evaporate the filtrate to dryness with hydrochloric acid and bake at 110° C. to deposit the last traces of silica. Ignite the residue in a weighed platinum crucible. If the residue is small, burn it with the paper; if it is large, burn them separately.

The residue consists of silica and clay. Treat it with 5 ml. of hydrofluoric acid and a few drops of concentrated sulphuric acid, evaporate to dryness, and ignite; repeat until there is no further loss in weight. The loss in weight is the silica content, except when the residue is large. In that case the residue should be fused with sodium carbonate and its silica content determined (p. 276). If the residue from the

silica is small, it can be either neglected altogether or fused with five to six times its weight of potassium bisulphate. The melt should then be dissolved in dilute hydrochloric acid, and this solution should be added to the filtrate from the silica.

*Note.* If the percentage of silicious matter is greater than 5, it is better to treat the carbonate as an insoluble silicate, and to determine silica by the method given on p. 274.

**Ferric Oxide and Alumina.** Add a considerable quantity of ammonium chloride solution, followed by ammonium hydroxide in very slight excess. If any ferrous iron is present, oxidise it by adding a little bromine water to the filtrate and washings from the silica determination, and remove the excess of bromine by boiling. Heat the solution nearly to boiling, and filter.

Wash the precipitate of aluminium and iron hydroxides twice with hot water: dissolve it in hot, dilute hydrochloric acid, and reprecipitate the iron and aluminium hydroxides by the addition of ammonium hydroxide in slight excess.

This second precipitation separates any calcium, which may be precipitated as carbonate (with the iron and aluminium hydroxides), by the ammonium carbonate which may be present in the ammonium hydroxide.

Filter, and wash with the precipitate with a hot, 2 per cent. solution of ammonium chloride. Mix together all these filtrates and washings.

Dry the precipitate in a steam-oven, and ignite the paper and the precipitate together at a bright red heat in a platinum crucible. Weigh the ignited residue of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . Retain this residue, if necessary, for the determination of the iron and the aluminium (see below).

If the limestone contained phosphate, the iron and ammonium will have been precipitated partially as phosphates. The phosphorus in the original material must be determined, and a suitable allowance must be made for it (pp. 77 or 136).

**Determination of Iron and of Aluminium by Difference.** The ignited and weight of solid hot, dilute, ly; e.g., by reduction with stannous chloride followed by titration with standard potassium of the  $\text{Al}_2\text{O}_3$ .

solution.

**Manganese.** If only a trace of manganese is present in the limestone, its determination may be neglected, since it will be precipitated with the iron and will cause no appreciable error in the weight of  $\text{Fe}_2\text{O}_3$  obtained. If, however, there is an appreciable quantity of manganese present, the iron and aluminium

must first be precipitated as basic acetates (p. 303); the manganese is then precipitated from the filtrate as hydrated dioxide, which is dissolved in hydrochloric acid and determined volumetrically by the bismuthate process (p. 267). The dioxide may be precipitated by the addition of ammonium hydroxide and bromine to the basic acetate filtrate.

**Calcium.** Mix together the ammoniacal filtrates and washings from the iron and aluminium precipitate, add 30 ml. of 50 per cent. ammonia solution, heat the liquid to boiling, and add a moderate excess of ammonium oxalate (p. 70). Filter, and wash the precipitated calcium oxalate two or three times. Dissolve the precipitate in hot dilute hydrochloric acid: filter if necessary, and reprecipitate the calcium oxalate by adding a slight excess of ammonium hydroxide solution, together with a few drops of ammonium oxalate solution. Filter; wash, dry, and ignite the precipitate, and weigh the calcium as oxide, or determine the calcium oxalate volumetrically with standard permanganate (p. 157).

The excess of ammonium salts retains most of the magnesium in solution, but if much magnesium is present, reprecipitation is necessary to remove this metal from the precipitate of calcium oxalate.

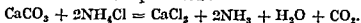
**Magnesium.** Pour the filtrates and washings from the calcium oxalate precipitation into a covered porcelain dish of diameter 15 cm. Add 20 ml. of concentrated nitric acid (or 3 ml. of nitric acid for every gramme of ammonium chloride present, if the latter quantity is known), to facilitate the removal of the ammonia. Heat the liquid, remove the cover when the vigorous evolution of gases has ceased, and evaporate the liquid to dryness, lightly greasing the inside edge of the dish to prevent the solution from creeping over. As soon as all the liquid has been driven off, place the dish on a sand-bath or on a piece of wire gauze, and heat to remove ammonium salts which prevent the complete precipitation of magnesium. Treat the residue in the cooled dish with a little concentrated hydrochloric acid; warm, add water, and filter if necessary. Proceed as described on p. 76.

**Alkali Metals.** Four grammes of the dolomite are powdered very finely in an agate mortar. The carbonate is dried and accurately weighed. It is mixed with 1 gm. of pure ammonium chloride and some 4 gm. of precipitated calcium carbonate (which is much more active than the natural material) by rubbing these compounds with the limestone in a mortar. The mixture is transferred to a large platinum crucible or to a special platinum thimble. The bottom of the vessel should first have been lined with a little of the precipitated carbonate. The crucible should have a capacity of some 30 ml., and the thimble be about 8 cm. long and 1.5 cm. wide at the mouth. The residue in the mortar is ground with successive quantities, about 1 gm. in all, of the precipitated carbonate, and transferred to the top of the platinum vessel. The vessel should be covered with a lid which fits tightly.

It is necessary to run a blank in parallel, using 1 gm. of the ammonium chloride and the same weight of precipitated chalk as used in the assay.

The crucible is placed in a hole in an asbestos sheet (or the thimble in its special holder), and heated gently for about fifteen minutes until the odour of ammonia can no longer be detected; but at no time should the

temperature be high enough to volatilise the ammonium chloride. During this period, calcium chloride is produced :



The temperature is then raised gradually until the bottom of the crucible is at a bright red heat, and this temperature is maintained for an hour. During this time, any silicates present are attacked, with the formation of calcium silicate and sodium and potassium chlorides. As these latter salts are appreciably volatile at a bright red heat, it is important to see that the lid of the crucible does not get too hot. The crucible is allowed to cool, and the sintered cake is gently removed from it and transferred to a large porcelain dish. A few drops of water are added and this cake is slowly slaked. Some 50 ml. of lime water are added and the dish is heated on a water-bath and the mass broken up with a glass rod. The purpose of the lime water is to prevent the magnesium from going into solution.

The liquid is decanted through a paper into a porcelain dish. The digestion of the mass in the dish with quantities of 50 ml. of lime water is repeated four times and the residue on the paper is washed with 50 ml. of a boiling, saturated solution of slaked lime. It is well to test the residue with hydrochloric acid. If it dissolves easily, leaving no grit, the decomposition of the dolomite has been complete.

The filtrate is boiled and the calcium is precipitated by adding ammonium hydroxide and ammonium carbonate. This precipitate should be collected, washed, dissolved in hydrochloric acid and reprecipitated, the runnings being added to the first filtrate. The filtrate from the calcium is evaporated to dryness and baked to drive off the ammonium salts. The residue is dissolved in a small volume of water and treated with a few drops of ammonium hydroxide and ammonium oxalate solution to remove the last traces of calcium. This precipitate is filtered off and the filtrate is evaporated to dryness in a small, weighed platinum or porcelain dish, and heated to a dull red heat. The cooled residue is treated with a drop of hydrochloric acid and reheated very slowly, again to a dull red heat. The residue gives the weight of the  $\text{NaCl} + \text{KCl}$ .

The residue in the dish may be extracted with water to make sure that it is all alkali salt, but the solution must be kept.

The Proportions of the Sodium and Potassium Chlorides which are present in this residue may be determined by one of the following methods, (a), (b) or (c); but the total weight of the chlorides is often simply reported as "alkalis."

(a) The weighed residue is dissolved in water, a few drops of  $\text{HCl}$  and an excess of platinic chloride are added, and the potassium is determined as  $\text{K}_2\text{PtCl}_6$  (p. 80). The corresponding weight of potassium chloride is now calculated, and the weight of the sodium chloride is found by difference.

(b) The weighed residue is moistened with concentrated  $\text{HCl}$  and dissolved in a small quantity of water, and the potassium is determined as  $\text{KClO}_4$  (p. 82).

(c) The weighed residue of the chlorides is dissolved in water, and the weight of chlorine present is determined by titration with standard silver nitrate solution.

The weights of sodium and of potassium present in the residue may be calculated as follows :

If  $x$  . . . . .  
 $y$  . . . . .  
 $a$  . . . . .  
 $b$  . . . . .

then :

$$(1) \quad x + y = a;$$

$$\text{and } \frac{\text{Cl}}{\text{NaCl}} x + \frac{\text{Cl}}{\text{KCl}} y = b, \text{ or } \frac{35.46}{58.5} x + \frac{35.46}{74.6} y = b;$$

$$\text{whence } (2) \quad 0.606 x + 0.475 y = b.$$

Multiplying equation (1) by 0.606 :

$$(3) \quad 0.606 x + 0.606 y = 0.606 a.$$

Subtracting (2) from (3) :

$$\begin{aligned} 0.131 y &= 0.606 a - b; \\ \text{or } y &= \frac{0.606 a - b}{0.131} \end{aligned}$$

And from equation (1) :

$$x = a - y = \frac{b - 0.475 a}{0.131}$$

It is customary to return the results in terms of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

Method (c) gives accurate results only when the sodium and potassium are present in approximately molecular proportions. It is useless for small quantities of sodium in the presence of large quantities of potassium or *vice versa*.

Limestone may also contain Phosphate, Sulphate, Sulphide, Chloride and Carbonaceous Matter. The phosphate may be determined in the manner described on p. 77 or on p. 138.

The total sulphur can be determined by weighing out 5 grm. of the limestone into an evaporating-basin. After the material has been made thoroughly wet by swilling it round with water, 2 ml. of liquid bromine are added. After ten minutes, 20 ml. of 10% sodium hydroxide solution is added. The solution is removed by :

If the treatment is continued, the sulphate will be given by this process.

The amount of sulphur present in the limestone can be determined by the method described on p. 138.

material. If the  $\text{CO}_2$  present as carbonate has already been determined (p. 85), the percentage of other carbon in the limestone can be calculated.

**Free Lime (Searle method).** This determination is particularly important with

previously used, is added ( $x$  ml.). Any lumps are broken up (by means of a glass



Evaporate to dryness once and bake at  $110^{\circ}\text{C}$ . Extract the chlorides with hydrochloric acid, and filter and wash the precipitate. Ignite it in a weighed platinum crucible and treat it with hydrofluoric and sulphuric acids. If there is now an appreciable residue, the silicate has not been completely attacked by the hydrochloric acid. Therefore a fresh portion of the silicate must be fused with sodium carbonate.

**Soluble Silica.** In order to distinguish between "soluble silica" (the combined silica which was present in silicates which have been decomposed by the hydrochloric acid) and "insoluble silica" (which was originally present in the free state in the substance), treat the silica precipitate in a large platinum dish for one hour at  $100^{\circ}\text{C}$ . with a 5 per cent. solution of sodium carbonate. The soluble silica is dissolved. Collect the insoluble silica and wash, ignite and weigh it.

The result obtained may not be absolutely correct, because a small quantity of the "insoluble silica" may also be dissolved by the carbonate.

**Other Elements.** If manganese is absent, the iron, aluminium, calcium, etc., are determined in the filtrate from the silica by the methods described on pp. 270 *et seq*.

If manganese is present in appreciable quantity, the iron and aluminium are separated by the basic acetate process (p. 300). The manganese is separated as sulphide (p. 278; see also p. 270), and the calcium and magnesium are determined as oxalate and pyrophosphate, respectively.

The manganese is determined colorimetrically in a fresh portion of the silicate.

Phosphates are determined by the ammonium molybdate process (pp. 77 and 136); or as magnesium pyrophosphate, after separation as phosphomolybdate (p. 78); and sulphur as sulphate (p. 65).

For some Results obtained by the Analysis of Lime, Mortar and Cement, see Tables V. and VI., pp. 403 and 404.

### Analysis of Insoluble Silicates

such as beryl, which contains beryllium, and petalite, which contains lithium, will be found in special treatises (p. 519).

Practice in the analysis of an insoluble silicate may be obtained by analysing orthoclase (potash felspar).

**Preparation of the Silicate.** Powder very finely about 5 grm. of potash felspar in the following way: Break the rock into coarse fragments with a hammer on a polished anvil. Next, powder these fragments in a percussion mortar (Fig. 19, p. 23), and finally grind the particles so obtained in an agate mortar until they are converted into an impalpable powder. The success of the analysis largely depends upon the careful reduction of the substance to a powder, which can only be considered as suitable when it passes entirely through a B.S. 150-sieve.

For some purposes it is desirable to start with the silicate in a standard state with respect to water. One method of doing this is to air-dry it



(p. 256) and then to dry it in an oven at  $105^{\circ}\text{C}$ . for one hour. A pair of clipped watch-glasses (Fig. 7, p. 11) will here be found useful. The loss in weight at  $105^{\circ}\text{C}$ . is a measure of the hygroscopic water.

**Treatment with Fused Sodium Carbonate.** Place about 5 gm. of anhydrous sodium carbonate in a platinum crucible which has a capacity of about 25 ml. Add an accurately-weighed quantity of about 1 gm. of the finely-powdered felspar. Mix these powders by means of a warmed, smooth, rounded glass rod, and cover the mixture with a seal of about 1 gm. of the carbonate. Note the total weight of the carbonate used.

Place the lid on the crucible, and heat it gently over a Bunsen flame. Gradually increase the temperature, taking care that no loss arises from the frothing which is caused by the evolution of carbon dioxide gas. The crucible is kept at a bright red heat for at least fifteen minutes after the mass has fused, until effervescence ceases and the fused mass becomes tranquil. If a muffle furnace is available it is convenient to use it for the fusion. The crucible and its contents are first placed at the mouth of the furnace, to warm up slowly, and then moved slowly inwards. Care must be taken to ensure that the atmosphere in the muffle is oxidising. A stream of air should always be passing through the heated chamber.

A blank fusion should be carried out, using the same quantity of sodium carbonate, under the same conditions as are used for the sample in every detail.

**Solution of the Metals.** When the fused mass is tranquil take up the crucible in a pair of platinum-tipped, or clean iron, tongs, and swirl the contents round until they have solidified. Then dip the hot crucible into cold water to detach the melt from the sides. The water should not enter the crucible (see p. 67).

If possible, withdraw the mass from the crucible and place it together with the crucible and lid, in a large porcelain basin and add some water. Slowly add 1 : 1 hydrochloric acid, keeping the dish covered with a clock-glass as much as possible, to guard against loss by effervescence. As soon as the platinum is clean, withdraw it, and hasten the disintegration of the silicate mass by breaking it up with a glass rod having a rounded end.

If any gritty particles are felt when the bottom of the vessel is stirred with a glass rod, the decomposition of the silicate has been incomplete. This is probably due to the original substance not having been sufficiently finely powdered. In this case start afresh. Use a more finely-powdered sample of the rock and raise the temperature of the crucible more slowly.

**Silica.** The acid liquid containing the silica is evaporated to dryness on a water-bath. The operation will necessarily take a long time and there may be a definite probability that fortuitous silicious matter will fall into the dish. In this case an inverted filter-funnel of diameter much larger than that of the dish should be held over it in such a way that the dish is partially within the funnel. Not only does the funnel act as a protection, but also it may cause a current of air to be drawn over the liquid and so hasten evaporation. As soon as the contents of the dish become thick and pasty, they should be continually stirred with a rounded glass rod in order to prevent the formation of lumps.

When all the liquid has been driven off, the dish is allowed to cool, and its contents are moistened with 10 ml. of concentrated hydrochloric acid and 100 ml. of hot water. When adding these liquids, it is well to cover the dish partially by a clock-glass to prevent the expulsion of the dust-like silica. Then allow the dish to stand on the water-bath for fifteen minutes; its contents should be stirred occasionally. If lumps are present, they should be broken up with a clean pestle.

Filter through Swedish filter-paper, wash with hot, dilute hydrochloric acid and finally with hot water, until the filtrate is free from chloride. Retain the paper with the precipitate. The filtrates should have been collected in a large porcelain dish. They will still contain a fairly large percentage of the silica. Evaporate them to dryness and bake the dish in an air-oven at  $110^{\circ}\text{C}$ . for one hour to dehydrate the silica. If a temperature much higher than  $110^{\circ}\text{C}$ . is used, there is some danger of the silica reacting with the chlorides present. Add 5 ml. of concentrated hydrochloric acid and 100 ml. of water to the cooled residue, and heat again on a water-bath. Filter through a small paper, washing with cold, dilute hydrochloric acid, and finally with cold water until free from chlorides. If great accuracy is required, the above treatment must be repeated, when a third, very small, yield of silica may result.

Ignite the papers, which need not be dried, with the precipitates in a platinum crucible to constant weight; remember that, as the powdered silica is probably hygroscopic, the covered crucible must be weighed quickly and that it must be cooled in an efficient desiccator prior to weighing. Then remove the silica by treatment with hydrofluoric and sulphuric acids, igniting the crucible and residue, and determine the difference (p. 100). Fuse the residue with potassium bisulphate and extract the melt with water, adding the solution from the silica filtrate (p. 269).

**Iron, Aluminium, Calcium and Magnesium.** The methods are given under Limestone (pp. 270-271).

**Alkali Metals.** Since the silicate has been treated with hydrofluoric acid, the alkali metals cannot be determined in the filtrate from the felspar. A separate portion of the felspar must accordingly be treated by the method is that of Lawrence Smith (p. 271). The filtrate from this is suitable for the determination of the alkali metals. The finely-powdered rock is mixed with a 1 gm. of precipitated calcium carbonate and 7 gm. of precipitated calcium carbonate. The mixture, after mixing is carried out is cleaned with a further 1 gm. of precipitated calcium carbonate.

For some Results obtained by the Analysis of the above glass, refer to Tables III. and V., pp. 491 and 492.

### Analysis of the

The principal constituents of ordinary glass are silica, soda, and calcium, but aluminium, iron, and boron may also be present. Common glass, therefore, is a silicate of soda, calcium, and boron. It is found in a naturally-occurring form, as in the case of flint glass, and boron is indeed, so great is the variety of

types of glass that a preliminary qualitative examination should always be made and a scheme of analysis formulated to suit the characteristics of an individual sample. The following notes may be of use in the preparation of such a scheme.

Prepare the glass for analysis and determine the silica in it by exactly the same methods as are used for the analysis of insoluble silicates (p. 275), except that about 0.5 gm. of potassium chlorate should be mixed with the glass-powder and the sodium carbonate, before the fusion is made.

Boron, if present, will be in the filtrate from the silica, from which it must be removed before other elements can be determined. This is done by adding 25 ml. of methyl alcohol to the solution of the fused mass in hydrochloric acid, every time that the solution is being evaporated to dryness to dehydrate the silica.

Lead is determined in the boron-free filtrate from the silica as follows: Add 1 drop of methyl orange to the solution and neutralise it with sodium hydroxide. Then add 2 or 3 drops of dilute hydrochloric acid. Saturate the solution with hydrogen sulphide, and collect the lead sulphide in a Gooch crucible. Wash the precipitate with water saturated with  $H_2S$ , and dilute the filtrate, again passing  $H_2S$  through it to ensure complete precipitation of the lead. Dissolve the lead sulphide in warm, 20 per cent. by volume nitric acid, and filter to remove the asbestos. Determine the lead in the clear solution as  $PbSO_4$  (p. 74).

Boil the filtrate from the  $PbS$  until the excess of hydrogen sulphide has been removed. If manganese is absent, precipitate the iron and aluminium, after oxidation of the iron with nitric acid, with ammonia in the presence of much ammonium chloride; if manganese is present, precipitate the iron and aluminium as basic acetates (p. 300). Ignite the precipitate and weigh the metals as oxides, examining the precipitate further, if necessary by the method given on p. 270.

Calcium and Magnesium can be determined directly in the filtrate from the iron and aluminium, provided Group IV metals are absent (pp. 270 and 271). If these metals are present, they must be removed before the calcium is precipitated by adjusting the ammonium hydroxide content of the filtrate until it contains about 10 ml. of 4 N. ammonia, saturating with  $H_2S$ , adding a further 10 ml. of 4 N. ammonia, stoppering the flask, and filtering after twelve hours. The precipitate of manganese and other sulphides must be washed with a dilute, colourless solution of ammonium sulphide. These sulphides are appreciably soluble in a solution of yellow ammonium sulphide.

Manganese is best determined colorimetrically (p. 240) in a fresh portion of the sample, which must be "opened up" by fusion with sodium carbonate and potassium chlorate.

**Alkali Metals.** Weigh out accurately about 1 gm. of the finely-powdered glass into a large platinum crucible, and digest it with 2 gm. of oxalic acid crystals and 20 ml. of 50 per cent. hydrofluoric acid. Evaporate the liquid to dryness. The silica is thus removed and the metals present are

converted to the oxalates. Heat the crucible just hot enough to expel the excess of oxalic acid. Cool, add 10 ml. of water and 1.5 gm. of oxalic acid. Repeat the evaporation and heating. This process should be repeated once more, using the same volume of water and the same weight of oxalic acid.

Treat the residue with hot water and filter off the lead and calcium oxalates; the alkali oxalates will be in the filtrate. Evaporate the latter to dryness and heat to convert the oxalates into carbonates. Treat the residue of the alkali salts with more hot water, and filter off any insoluble carbonates. Evaporate the filtrate to dryness with hydrochloric acid to remove the last traces of silica. Treat the residue with dilute hydrochloric acid, filter and evaporate to dryness. The contents of the crucible will now be sodium and potassium chlorides only. Weigh this residue, and determine the potassium as perchlorate (pp. 80 and 82).

**Boron.** Fuse 0.5 gm. of the finely-powdered glass with six times its weight of anhydrous sodium carbonate.

(a) *Gravimetric Determination of  $B_2O_3$ .* The fused mass is allowed to cool and is extracted with water, and the solution is filtered and evaporated to a small volume. The filtrate, which contains the borate, is acidified as is described on p. 102, and is transferred, with any silica which separates, to the retort A (Fig. 68, p. 103), and the  $B_2O_3$  is determined as directed.

(b) *Volumetric Determination of  $B_2O_3$ .* Treat the cool mass, resulting from the fusion, with 25 ml. of 50 per cent. hydrochloric acid, add a few drops of  $HNO_3$  to oxidise any ferrous iron which may be present, and place the liquid in a 250-ml., round-bottomed flask. Heat the contents of the flask nearly to boiling, add dry, precipitated  $CaCO_3$  in moderate excess, and boil vigorously under a reflux condenser for about ten minutes to destroy bicarbonate and to precipitate the  $Al_2O_3$  and  $Fe_2O_3$  completely; the condenser will return the slightly-volatile boric acid to the flask. Filter through a small Buchner funnel, and wash the precipitate several times with hot water, keeping the total volume of liquid below 100 ml. Return the filtrate to the flask, add a little  $CaCO_3$ , and heat nearly to boiling. Take away the burner, and remove the last traces of  $CO_2$  by connecting the flask with a filter-pump, through a trap, and continuing the suction until the boiling has nearly ceased. If the liquid is reddish in colour, ferric hydroxide is probably present and must be removed by filtration.

The boric acid can now be determined. Add a few drops of phenolphthalein to the contents of the flask, and titrate with decinormal sodium hydroxide until the liquid is distinctly pink. Then add 1 gm. of mannitol or 10 ml. of glycerol, when the colour will disappear. Continue the titration until the pink colour returns. Make sure that this end-point is genuine by adding a second, or perhaps even a third, portion of mannitol or glycerol; the volume of the sodium hydroxide necessary to cause the return of the colour will serve as a guide to the number of portions it is desirable to add. From the volume of standard NaOH solution used, calculate the weight of  $B_2O_3$  present (p. 132).

### Analysis of Zinc-Blende

Zinc-blende consists essentially of zinc sulphide, which is, however, commonly associated with galena or lead sulphide, and occasionally with calamine or zinc carbonate. The ore may also contain iron, aluminium, manganese, copper, cadmium, and other metals.

**Moisture.** The moisture is usually adherent only, and is not combined; it can therefore be determined by drying at  $105^{\circ}\text{C}$ .

**Solution of the Ore.** "Open up" the ore with hydrochloric and nitric acids, and fume with sulphuric acid as is described on p. 261.

**Determination of Silica and Lead.** After cooling the dish, dilute its contents with water and filter. Wash the residue on the paper with water containing a few drops of sulphuric acid, and finally with methylated spirit until all the acid has been removed. Add the first washings to the filtrate and keep this liquid, but reject the alcoholic washings.

The solid residue consists of gangue or earthy matter, silica, and lead sulphate; dry it in the steam-oven, ignite it apart from the filter, and weigh it after converting any lead, which has been reduced by the burning paper, into sulphate (p. 74). Dissolve out the lead sulphate from this residue by boiling it with strong ammonium acetate solution made alkaline with ammonium hydroxide. Repeat this treatment with fresh portions of the solvent until no lead can be detected in a drop of the acetate solution, when it is tested with a solution of potassium dichromate. Again dry the residue, and ignite and weigh it. The loss of weight on extraction with the ammonium acetate solution represents the lead sulphate which the residue contained (see also "Lead in Galena," p. 282).

In exact analysis, the silicious matter, after the removal of the lead sulphate, should be treated with hydrofluoric acid, and the residue fused with potassium bisulphate; the melt is extracted with water and added to the original filtrate from the silica.

**Copper and Cadmium.** Separate these metals from the filtrate from the silica, as sulphides, following the directions given on p. 261. A portion of the filtrate and washings, after dilution, must be tested with hydrogen sulphide, in order to make sure that no copper remains in solution. This portion is subsequently added to the main filtrate.

If cadmium is present in the ore, dissolve the sulphide precipitate in dilute nitric acid, and remove the sulphuretted hydrogen and oxides of nitrogen by boiling. Determine the copper by electrolysis, using a solution in nitric acid (p. 230); or either gravimetrically (p. 61) or volumetrically (p. 182) as thiocyanate, after removing the nitric acid by fuming with sulphuric acid. If cadmium is absent, dry the sulphide

with  $\text{H}_2\text{S}$ , dissolve it in hydrochloric acid, transform it to sulphate, and weigh it as such (p. 95).

Alternatively, if the quantity of cadmium present is small, transfer the filter-paper containing the sulphide to a stoppered bottle. Add 200 ml. of air-free water, and shake the bottle violently to break up the paper and the precipitate. Add a few millilitres of dilute hydrochloric acid and, without waiting for the sulphide to dissolve, an excess of a standard solution of iodine :



**Titrate the excess of iodine with sodium thiosulphate, using starch as indicator.**

**Iron.** Boil the filtrate from the  $\text{CuS}$  until the hydrogen sulphide is removed. Then add nitric acid to oxidise the iron.

If manganese is absent, precipitate the iron as ferric hydroxide (p. 270); a double precipitation will be necessary. If manganese is present, precipitate the iron by the basic acetate method (p. 300), using a double precipitation if the precipitate is at all bulky. Filter, wash, dry and ignite the precipitate, and weigh the iron as  $\text{Fe}_2\text{O}_3$ ; or dissolve the precipitate in hot, 50 per cent., hydrochloric acid, reduce the iron with stannous chloride, and titrate it with standard potassium dichromate solution. This latter method is preferable.

**Manganese.** Roast the ore in an open dish to remove sulphur. Digest it for half an hour on a water-bath with 25 ml. of concentrated hydrochloric acid. Remove the hydrochloric acid completely by fuming with sulphuric acid. Cool, dilute somewhat, and filter. Add 30 ml. of concentrated nitric acid, and determine the manganese by the bismuthate process, first removing any oxidisable matter by a preliminary treatment with sodium bismuthate (p. 311).

**Zinc.** If manganese is absent, zinc may be determined directly in the filtrate from the iron. If the basic acetate separation for iron has been used, the manganese will be present with the zinc in the filtrate. It must be removed by adding an excess of bromine water, together with an excess of ammonium hydroxide, boiling, and removing the precipitate of manganese dioxide by filtration. Determine the zinc volumetrically with ferrocyanide, using uranium acetate as indicator (p. 199).

Alternatively, in the absence of Cu, Mn, Ni and Co, the zinc may conveniently be precipitated in the form of zinc pyridine thiocyanate,  $\text{Zn}(\text{CNS})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , as follows:—

cupboard) 1 to 15 drops of pyridine. Avoid too great an excess, as indicated by the formation of an oily layer and by the strong odour. Filter the cold mixture through a Gooch crucible, wash the precipitate with water, and dry it at 100° cent. each of pyridine,  $\text{NH}_4\text{CNS}$  matter, treat the residue with complete oxidation, and finally e it as  $\text{ZnO}$ .

Sulphur may be determined by any of the three methods given on p. 68 *et seq.*; preferably, fuse 0.5 grm. of the ore with sodium carbonate

and potassium nitrate. Extract the fused mass with water, acidify with nitric acid, and remove the elements which interfere with the determination of sulphur, namely, lead, iron and aluminium, by adding an excess of sodium carbonate solution and boiling for at least half an hour. Any lead sulphate will be changed into lead carbonate. Filter, and wash the residue. Acidify the filtrate and washings with dilute hydrochloric acid, and concentrate the solution by evaporation. Add concentrated hydrochloric acid in excess and evaporate to dryness to expel all nitric acid. Repeat the evaporation with hydrochloric acid, if this is thought to be necessary. Dissolve the residue in water which has been acidified with hydrochloric acid, filter if necessary, and determine the sulphur as barium sulphate (p. 68).

**Carbonate.** Heat 4 grm. of the finely-powdered ore with dilute sulphuric acid, in which some chromic anhydride has been dissolved; the carbon dioxide, which is evolved, is collected and weighed. The carbon dioxide is bubbled through a saturated solution of chromic anhydride to which a little dilute sulphuric acid has been added, before it passes into the soda-lime tubes. The chromic acid prevents the evolution of hydrogen sulphide and sulphur dioxide, which would also be absorbed.

For the Results of Analyses of Zinc-Blende and Zinc Concentrates, refer to Table IV., p. 492.

### Analysis of Galena

Galena consists essentially of lead sulphide; but it may also contain silicious matter, silver, copper, antimony, zinc and iron.

The determination of the percentage of silver is frequently of great importance. The amount is usually too small to be obtained accurately by precipitation, and dry assay methods (p. 340 *et seq.*) should be used.

**Moisture.** Weigh out accurately about 1.5 grm. of the finely-powdered ore, heat it at 105° C. to constant weight; collect the water given off. Usually very little moisture is present.

**Silica and Lead.** Weigh out about 1 grm. of the ore and digest it with 20 ml. of concentrated hydrochloric acid in a conical flask, in the neck of which a small funnel has been placed. When the reaction appears to be over, add successive small quantities of nitric acid and boil. No black specks of undecomposed ore should be left. Sometimes the solution of these black specks can be hastened by the cautious addition of about 1 ml. of bromine to the cooled liquid.

Transfer the solution and any residue to a basin, and evaporate it to dense white fumes with 5 ml. of concentrated sulphuric acid. Proceed as in the determination of lead in zinc-blende (p. 280). To ensure accuracy add dilute sulphuric acid in slight excess to the solution of the lead sulphate in ammonium acetate, and remove the acetic acid by evaporation. Determine the lead gravimetrically as lead sulphate (p. 74); or as lead chromate, either volumetrically (pp. 154 or 173) or gravimetrically (p. 74). If a chromate method is selected, the ammonium acetate need not be removed.

**Copper.** Dilute the filtrate from the lead to about 400 ml. and raise the sulphuric acid content to about 5 ml. per 100 ml. of solution. Heat to  $80^{\circ}\text{C}$ ., and saturate the solution with hydrogen sulphide. Allow the liquid to stand, and filter off the precipitated sulphides of copper and antimony. Wash the precipitate, as rapidly as possible with water containing hydrogen sulphide, and cover the funnel with a clock-glass so as not to expose the precipitate unnecessarily to oxidation by the atmosphere. Keep the filtrate and washings.

Dissolve 5 gm. of sodium sulphide in 50 ml. of water, using a small beaker. Add the paper containing the sulphide precipitate, and boil for about a minute. If the solution is yellow, sodium polysulphide, in which copper sulphide is soluble, will probably be present. Reduce the polysulphide to sulphide by the addition of a solution of sodium sulphite, using only a small excess. Dilute to 150 ml., and heat on a water-bath for half an hour. Collect the precipitate, which will be copper sulphide, and wash it with a dilute solution of sodium sulphide. The filtrate will contain the antimony. Dry the precipitate and ignite it, together with the paper, in an open dish. Determine the copper by one of the methods on p. 280.

**Antimony.** Acidify the sodium sulphide filtrate with hydrochloric acid and saturate it with  $\text{H}_2\text{S}$ . Collect and wash the precipitate of antimony sulphide, and either convert it to  $\text{Sb}_2\text{O}_3$  and weigh it as such (p. 95); or dissolve the sulphide in concentrated hydrochloric acid, boil off the  $\text{H}_2\text{S}$ , add 5 ml. of a saturated solution of  $\text{SO}_2$ , and enough sulphuric acid to bring the strength of that acid in the solution to 30 per cent. by volume. Boil off the excess of  $\text{SO}_2$ , dilute, cool to below  $10^{\circ}\text{C}$ . and titrate with a solution of potassium permanganate. The antimony solution to be titrated must contain about 10 per cent. by volume of hydrochloric acid and 10 per cent. by volume of sulphuric acid, and the permanganate must be standardised against a standard solution of antimony reduced in the same way. At the end-point, the pink tint of the permanganate will persist for ten seconds.

In the event of the titration being unsatisfactory, concentrate the spent liquor, reduce it again with  $\text{SO}_2$ , and repeat the determination.

**Iron and Aluminium.** Boil off the hydrogen sulphide from the original filtrate from the copper, add a few drops of bromine water to convert the iron into the ferric state and boil off the excess of bromine. Then add ammonium chloride solution and a slight excess of ammonium hydroxide. Filter, wash the precipitate twice, redissolve it in hydrochloric acid, and precipitate it again with ammonium hydroxide. Filter off the precipitate, dry and ignite it, and weigh as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . The determination of the iron in this precipitate has already been described (p. 270).

**Zinc.** Combine all the filtrates and washings from the iron and aluminium precipitate, and titrate them with dilute sulphuric acid until the solution is neutral to methyl red. Add sulphuric acid in excess to bring the content of the solution with respect to that acid to about centinormal. Pass a rapid stream of  $\text{H}_2\text{S}$  through the solution, which should be at room temperature, for thirty minutes. Allow the precipitate to settle. Filter



and wash the zinc sulphide with cold water. Dissolve it in 50 per cent. hydrochloric acid, boil off the  $H_2S$  and determine the zinc with ferrocyanide (p. 199). Precipitation with  $H_2S$  in the presence of a small quantity of mineral acid separates zinc from manganese, nickel and cobalt.

**Sulphur** is determined in the same way as is sulphur in zinc-blende (p. 281). Care must be taken to transform any lead sulphate produced into lead carbonate.

The sulphur in galena can also be determined accurately by heating the finely-powdered ore with iron powder. The iron sulphide produced is treated with hydrochloric acid, and the hydrogen sulphide is collected in hydrogen peroxide (p. 69).

For the Results of an Analysis of Lead Concentrates, refer to Table IV., p. 492.

### Analysis of Copper Pyrites

Copper pyrites is the commonest ore of copper. It consists essentially of a double sulphide of copper and iron, having the formula  $CuFeS_2$ . The ore, however, usually contains silicious matter and small quantities of lead, bismuth, arsenic, antimony, manganese, and zinc, and occasionally nickel and cobalt.

A qualitative analysis of the ore should always precede the quantitative determination.

**Moisture.** The finely-powdered pyrites is heated in a steam-oven until its weight becomes constant, or, better, in a tube at  $105^\circ C.$ , the water being collected. As some specimens of pyrites also lose sulphur at this temperature, care must be taken that none of this element is also collected and weighed.

**Insoluble Matter.** Weigh out accurately about 1 gram. of the ore into a porcelain evaporating-dish. Add 10 ml. of concentrated nitric acid which has been saturated with potassium chlorate, and allow the mixture to stand in the cold for fifteen minutes, the dish being covered with an inverted funnel to prevent loss by spiriting. Then heat on a water-bath, adding 10 ml. of concentrated hydrochloric acid in small quantities from time to time. As soon as all the sulphur, which separates out at first, is dissolved, transfer the dish to a hotplate, add 7 ml. of sulphuric acid, and evaporate the solution to dense white fumes in order to remove the nitric acid and to render the silica insoluble.

Dilute cautiously with some 75 ml. of water and heat until all the somewhat insoluble ferric sulphate has dissolved. Filter off and wash the residue, and retain the solution and washings. Determine the lead and silica in the residue in the way described under zinc-blende (p. 280).

**Copper.** Separate the copper from the filtrate from the insoluble residue by the use of aluminium foil (p. 262). Dissolve the copper in nitric acid and determine it iodometrically or electrolytically (p. 228).

**Arsenic.** Dissolve about 1 gram. of the ore in a mixture of nitric and hydrochloric acids, and remove the silica and lead (see above). Saturate

the hot, acid filtrate with hydrogen sulphide to precipitate the sulphides of copper, arsenic, and antimony, together with any traces of lead (p. 261). Wash the precipitate with hydrogen sulphide water and retain the filtrate.

Dissolve the arsenic and antimony sulphides in sodium sulphide (p. 283). Filter, and wash the paper with hydrogen sulphide water. Neglect the precipitate. Make the filtrate just acid with hydrochloric acid, and reprecipitate the arsenic and antimony by again saturating the solution with hydrogen sulphide. Filter, wash, and dissolve the sulphides in 1 : 1 HCl to which a few crystals of potassium chlorate have been added. The metals are then in the pentavalent state. Heat the solution on a water-bath until all chlorine has been expelled.

Dilute to about 100 ml., add 3 grm. of tartaric acid in solution, and 50 ml. of magnesia mixture (p. 78). Precipitate the arsenic as magnesium arsenate and determine it as magnesium pyroarsenate (p. 79).

*Note.* A little arsenic may be left in the solution and a little antimony may be precipitated with the arsenate, but the results are usually accurate enough for practical purposes. Information about more accurate methods, which are necessarily more elaborate, must be sought elsewhere.

**Antimony.** Reprecipitate the antimony in the filtrate from the arsenic once again with hydrogen sulphide. Convert the sulphide into  $\text{Sb}_2\text{O}_4$ , and weigh as this oxide (p. 95).

**Iron; Manganese, and Zinc.** These metals are determined in the acid solution from which the copper, arsenic and antimony have been removed as sulphides. The excess of hydrogen sulphide is removed by boiling, the iron is oxidised by nitric acid or by bromine water, and the elements are determined by the methods indicated under zinc-blende (p. 281). If the zinc is present in very small quantity, it should be precipitated from a very weakly acid solution as zinc sulphide, and determined as ferrocyanide (p. 199).

**Sulphur.** See under "Zinc-Blende" (p. 281).

The Results of Analyses of Copper, Iron and Burnt Pyrites are given in Table IV., p. 492.

### Analysis of Brass

Brass is an alloy consisting mainly of copper and zinc, but small quantities of lead, iron and other metals are usually present.

**Preparation of the Sample.** The sample for analysis should be removed with a drill, since, if a file is used, its teeth may be broken off and the proportion of iron in the filings consequently increased. If necessary, the sample can be passed between the poles of an electromagnet to remove iron which has been accidentally introduced.

Copper can be determined accurately and rapidly by electrolysis, using a rotating electrode (p. 229). This method is particularly to be recommended, because the lead can be determined at the same time (p. 233). When electrolytic apparatus is not available, the copper is best determined

volumetrically by the potassium-iodide-thiosulphate method (p. 177); or gravimetrically, as thiocyanate (p. 61).

**Lead and Tin.** The lead may be determined electrolytically as  $PbO_2$  by deposition on the anode at the same time as the copper is being deposited on the cathode (see above). Alternatively, dissolve about 7 gm. of the brass in the least possible quantity of 1 : 1 nitric acid, using a covered porcelain basin. When the action is over, evaporate just to dryness, moisten the residue with nitric acid, and add 50 ml. of hot water. When all the copper and zinc have dissolved, set the basin aside and allow the metastannic acid to settle. Collect this precipitate on a filter-paper, and treat it as described on p. 97, weighing as  $SnO_2$ . The precipitate will probably be contaminated, but if, as is generally the case, its total weight is small, this is unimportant. If considerable quantities of tin are present, determine the tin by the method given under "Bronze" (p. 287).

The filtrate from the tin should have been collected in an evaporating-dish. Add 15 ml. of concentrated sulphuric acid, and evaporate to dense white fumes. If the sample is to be used also for the determination of zinc, all nitric acid must be removed. A second evaporation, after the addition of dilute sulphuric acid, may therefore be necessary. Extract the cold contents of the dish with a hot solution containing 3 parts of water and 1 of alcohol, using no more of this solution than may be necessary. Allow the dish to stand for an hour, and then collect the insoluble lead sulphate in a Gooch crucible, wash it with dilute sulphuric acid and finally with alcohol, and ignite it at a dull red heat to constant weight, the Gooch crucible being placed on an asbestos pad in a larger nickel crucible. Alternatively, dissolve the lead sulphate in ammonium acetate, and determine the lead volumetrically by a chromate process (pp. 154 or 173).

**Zinc.** Most of the elements to be found in brass interfere with the determination of zinc and must be removed. If the zinc is determined in the solution from the lead, all alcohol must be removed by evaporation. Then make up the liquid to 250 ml., and take three 25-ml. portions. If a fresh sample is taken, weigh out three separate portions of about 0.6 gm., dissolve them in the least possible quantity of 1 : 1 nitric acid, using evaporating-dishes, add 10 ml. of concentrated sulphuric acid, and evaporate to dense white fumes. Cool, wash down the dish of dilute sulphuric acid, and again evaporate to white fumes. cool solutions and transfer them to beakers.

Bring the volume of the zinc solution, no matter how small, up to 100 ml., and make certain each portion contains 25 ml. of concentrated sulphuric acid. Pass hydrogen sulphide through which must have been heated at  $80^\circ C.$ , until the solution is completely precipitated of the copper is solution and the greatly increased fumes settle. Filter through a large filter-paper with hydrogen sulphide and containing 100 ml. per litre. It is well to keep both the funnel and the filtration, to avoid oxidation and con-  
For very exact work it is advisable to dry

to dissolve the oxide in acid, and to reprecipitate it as before. The small quantity of zinc adsorbed on the copper sulphide will thus be recovered.

Evaporate the filtrate from the copper until all traces of hydrogen sulphide have disappeared and until it has been much reduced in bulk. Add a little bromine water to oxidise the iron present, and boil off the excess of bromine. Add 10 grm. of ammonium chloride and make the solution alkaline with ammonia to precipitate the iron. Collect the ferric hydroxide, dissolve it in hydrochloric acid, precipitate it again with ammonia, and add the second filtrate to the first. This procedure is necessary because the first precipitate of ferric hydroxide will probably contain an appreciable quantity of zinc.

Determine the zinc in the solution volumetrically with a solution of  $K_4FeC_6N_6.3H_2O$  containing about 45 grm. of the crystals per litre, using uranium acetate as external indicator (p. 199). The ferrocyanide should be standardised either against a brass of known zinc content or against pure zinc.

**Iron.** The iron was precipitated as  $Fe(OH)_3$  when the zinc was determined. This precipitate can either be ignited and weighed as  $Fe_2O_3$ ; or dissolved in hydrochloric acid and titrated with titanous chloride or potassium dichromate. If the brass contains only traces of iron, this metal is best determined colorimetrically (p. 237).

The Composition of a Typical Brass is given in Table II., p. 491.

### Analysis of Bronze

Bronze is an alloy consisting chiefly of copper and tin, but zinc, iron, lead and other metals may also be present.

**Tin.** Dissolve 1 grm. of the alloy in 10 ml. of concentrated nitric acid in a covered, porcelain basin. When the action is over, evaporate slowly to dryness, and bake. As the  $SnO_2$  will be contaminated with other metals, it is well to ignore such contamination at this stage and to make sure, by baking well, that all the stannic oxide has been rendered insoluble. Add 100 ml. of hot water and 10 ml. of nitric acid, stir, and boil. Filter through a paper and wash the residue with hot water. Retain the filtrate and the washings.

Dry the paper and the precipitate carefully, and ignite them in a 2-inch diameter nickel crucible until the paper has been destroyed. A platinum crucible must not be used. Add a stick of sodium hydroxide, about 1.5 inches in length, and melt it gently over the residue. Finally, raise the temperature to dull red heat and maintain this temperature for five minutes. Swing the crucible as it is cooling to cause the liquid to mount up the sides, where it will solidify. Put the cold crucible, filled with water, into a beaker, and warm gently until the crucible appears to be clean. Persistent insoluble matter, if any, may be neglected. Transfer all the liquid to the beaker and wash out the crucible twice with concentrated hydrochloric acid.

Transfer the liquid to a reduction-flask and reduce the stannic chloride with nickel foil or with precipitated antimony (p. 183). The precautions against oxidation given before must be stringently observed, and care must be taken to see that the concentration of hydrochloric acid is not

allowed to become too low. Titrate the stannous chloride with standard iodine solution, or use one of the bromate methods (p. 182).

**Copper.** Dissolve about 0.5 gm. of the fine turnings in a mixture of 10 ml. of concentrated sulphuric acid, 30 ml. of water, and 5 ml. of concentrated nitric acid. When solution is complete, boil gently to expel any nitrous acid, but do not boil for a long time or metastannic acid contaminated with copper will be precipitated. If necessary, remove the last traces of nitrous acid by urea. Add ammonia cautiously until there is a slight, permanent precipitate. Then acidify with acetic acid. The precipitate of tin may not dissolve in the acetic acid. This is of little consequence. Make up the solution to a known volume, reduce the copper with potassium oxide, and titrate one-fifth with standard sodium thio-sulphate of approximately decinormal concentration.

The electrolytic method is particularly suitable for this determination. The solution of the alloy in a mixture of nitric and sulphuric acids is made as is described above. The nitrous acid is carefully removed and the solution is electrolysed, using a rotating platinum anode (p. 230).

**Phosphorus.** Dissolve about 1 gm. of the fine turnings in a mixture of 10 ml. of concentrated hydrochloric and 10 ml. of concentrated nitric acid, and evaporate just to dryness. Cool, and add about 7 ml. of concentrated hydrochloric acid. Heat until the residue has dissolved, and then dilute the solution with cold water. Add a small piece of zinc rod, on which the copper and tin will be precipitated, leaving the phosphorus, as phosphoric acid, in the solution. Filter. Wash the precipitate once with hydrochloric acid diluted with its own volume of water, using not more than 10 ml. of this solution; and then with hot water until the filtrate is free from chlorides.

Add 2 drops of concentrated nitric acid and 10 ml. of a solution of ferric chloride of reagent concentration (p. 517) to the boiling solution and then add ammonia until the solution is alkaline. The phosphorus will be precipitated as ferric phosphate. Collect the precipitate on a filter, wash it. Dissolve it again by pouring about 40 ml. of nitric acid (1 volume of acid, three volumes of water) over the paper. Boil. Add ammonia (sp. gr. 0.880) to the solution, and then precipitate the phosphorus as ammonium phosphomolybdate (p. 77). Determine the phosphorus by weighing this precipitate (p. 78), or volumetrically (p. 136) with 10 ml. of standard solution, and accurately, as magnesium pyrophosphate (p. 77).

**Minor Constituents of Bronze.** The filtrate and washings from the phosphorus will contain most of the lead, zinc, iron and copper present in the alloy. The first three of these metals can be determined in this filtrate as described for brass (p. 286). The copper must be removed before the lead and zinc are determined. The small quantities of lead, zinc, and iron retained by the stannic oxide when the tin was removed may be determined by the method of p. 491.

The Composition of a Typical Bronze is given in Table II., p. 491.

### Analysis of German Silver

German silver is an alloy of copper, zinc, and nickel, and frequently contains traces of tin and iron. The sample for analysis should be in a state of division, as millings or drillings.

**Tin and Copper.** Proceed exactly as is directed under "Brass" (p. 285). For the copper, dissolve the metal in nitric acid, remove tin, if present, by evaporation to dryness and filtration, convert the nitrates to sulphates by evaporation of the filtrate with sulphuric acid, and determine the copper gravimetrically as cuprous thiocyanate (p. 61).

**Iron.** Dissolve 0.5 gm. of the alloy in nitric acid and convert the nitrates to sulphates by treatment with concentrated sulphuric acid. Remove the copper and tin as sulphides, and precipitate the iron with ammonia as described under "Brass" (p. 285). A double precipitation of the iron will probably be necessary.

**Nickel.** Make the filtrate from the iron just acidic with hydrochloric acid, and then just alkaline with ammonia. Precipitate the nickel with dimethylglyoxime (p. 62).

**Zinc.** Acidify the filtrate from the nickel with hydrochloric acid, and boil it vigorously to expel most of the alcohol and to destroy the excess of the dimethylglyoxime reagent. Add ammonia until the liquid is nearly neutral, and determine the zinc as described on p. 75.

### Analysis of Cupro-Nickel Alloys

These alloys contain copper and nickel in widely varying proportions, together with an appreciable quantity of manganese and, say, 0.2 per cent. of other elements, of which the most important are silicon, carbon and iron.

**Copper and Nickel.** It is convenient to determine these metals by the use of salicylaldoxime,  $C_7H_7O_2N$ , with which both these metals form complexes,  $(C_7H_7O_2N)_2Cu$ —18.94 per cent. Cu, and  $(C_7H_7O_2N)_2Ni$ —17.74 per cent. Ni. The nickel complex is soluble and the copper compound is insoluble in weakly acidic solutions; the nickel compound is insoluble in weakly alkaline solutions. Hence they can be separated. The other elements probably present will not interfere, though cobalt would be precipitated with the nickel.

To prepare a solution of the reagent, dissolve 1 gm. of salicylaldoxime in 5 ml. of alcohol and dilute to 100 ml. with warm water, with agitation. Alternatively, prepare the solution from salicylaldehyde and hydroxylamine as follows: Dissolve 2.22 gm. of salicylaldehyde in 8 ml. of ethyl alcohol, and dissolve 1.17 gm. of hydroxylamine hydrochloride in 2 ml. of water. Mix the two solutions and add 15 ml. of ethyl alcohol. Stir this solution slowly into 225 ml. of water which have been heated to 70° C. If a precipitate appears on cooling, allow the solution to stand for two hours and then filter it. If properly made, this solution will contain about 1 gm. of the oxime in 100 ml.

To carry out the determination, dissolve about 0.12 gm. of the millings or fine drillings in the least possible quantity of nitric acid, using a beaker. Expel all nitrous fumes by boiling. Make the solution just alkaline with ammonia and dilute it to 20 ml. Add 1.2 gm. of sodium acetate, and 10 ml. of glacial acetic acid. Then add, while stirring, 100 ml. of the reagent solution to the solution of the alloy, which must be cold.

Continue to stir until the precipitate of the copper compound has coagulated well, and then collect it in a weighed Gooch or sintered glass crucible. Wash the green compound with cold water until a drop or two of the filtrate fails to give a purple colour with a solution of ferric chloride, and dry it at  $100^{\circ}$  to  $105^{\circ}$  C.

Add dilute ammonia to the filtrate until the solution is definitely alkaline, but not in such quantity that a drop of it will give a red colour with a drop of phenolphthalein, when tested on a white tile. During this operation the solution must be stirred. When the nickel compound has coagulated, collect, wash, and dry it in the same way as the copper precipitate was treated.

**Minor Constituents.** For manganese, silicon and carbon use the methods described under steel (pp. 309, 311 and 304, respectively). For manganese, a sample weighing 2 grm. may prove suitable, but, as the percentages of silicon and carbon are probably very small, much larger quantities of alloy must be taken for their determination.

To determine the iron, dissolve 5 grm. of the alloy in nitric acid. Dilute the solution, add ammonium chloride to it, and precipitate the iron with ammonia. Dissolve the ferric hydroxide in hydrochloric acid and again precipitate the iron, this time by the basic acetate process (p. 300). Weigh it either as ferric oxide, or determine it by the colorimetric method (p. 237).

An Analysis of a Cupro-Nickel Alloy is given in Table II., p. 491.

### Analysis of White Metals

Alloys containing large percentages of lead or tin are generally referred to as "white metals." This group contains a very large number of alloys, such, for example, as plumber's solder (often 3 parts of lead and 2 of tin, with some antimony), pewter (4 parts of tin and 1 of lead, sometimes with antimony), type-metal (approximately 7 lead, 2 antimony, 1 tin, sometimes with copper), the various tin-base and lead-base bearing metals, and the fusible alloys. Some of these alloys contain a considerable number of elements and the analysis is difficult and complicated. The analysis of metal containing only tin, lead, antimony and copper is discussed here. For further information, consult Scott's *Standard Methods of Chemical Analysis*, Vol. II.

**Antimony.** Take 2 grm. of alloy or that weight of alloy which is judged to contain 0.1 grm. of antimony, whichever is the smaller, in a conical flask. The metal must be in the form of thin foil or be otherwise in a state of fine division. Add 20 ml. of concentrated sulphuric acid and 5 grm. of potassium bisulphate to raise the boiling-point of the liquid, and heat vigorously until the sample has disintegrated. Allow the acid to fume strongly for five minutes. After the flask has cooled, add 10 ml. of water very cautiously, and 5 ml. of concentrated hydrochloric acid. Boil the solution gently for five minutes. The antimony should now all be in solution in the trivalent state, and the tin exclusively in the stannic form. Dilute to 150 ml. with water, cool to  $10^{\circ}$  C., and titrate with approximately 0.05 N. potassium permanganate until the pink tint is permanent for twenty seconds. Standardise the permanganate against

portions of 0.1 grm. of pure antimony which have been treated in the same way as the alloy.

*Note.* In the case of alloys containing small quantities of  $\alpha$  with  $\text{SO}_2$ , cool to  $10^\circ$ .

**Tin.** Take that weight of the alloy which contains about 0.15 grm. of tin, but do not use more than 3 grm. of the sample. Use the solution from the antimony, or, better, dissolve a fresh portion in 20 ml. of concentrated hydrochloric acid, to which it may be necessary from time to time to add bromine. All the metal must be disintegrated. If the solution is boiled, some of the volatile stannic chloride may be lost. If a considerable excess of bromine remains after the action is over, reduce the amount by the careful addition of sulphurous acid. As the acid must on no account be added in excess, enough bromine to give a definite straw tint to the solution must be left.

The tin must now be reduced and titrated with iodine (p. 165). Transfer the solution, however it has been prepared, to the reduction-flask, adjust the concentration of hydrochloric acid, and reduce with nickel foil or precipitated antimony, observing all the precautions against oxidation advised on p. 183. Titrate with approximately 0.1 N. iodine, which is best standardised by weighing out quantities of the metals similar to those taken in the alloy, but without melting them together, and treating them exactly as the alloy has been treated.

Copper, if present in considerable quantity, interferes with this determination, but only if the iodine is added rapidly. Consequently, add the iodine drop by drop to the solution, which should be in rapid movement to avoid a high local excess of iodine. If the end point is poor, reduce the tin and titrate it again.

**Lead.** *First Method*, to be used when copper also is to be determined, Dissolve 1 grm. of the finely-divided alloy in 100 ml. of a mixture consisting of five volumes of water, four of concentrated hydrochloric acid and one of concentrated nitric acid, to which 2 grm. of potassium chloride have been added. Use a covered beaker. When all the metal has dissolved, remove the cover, evaporate to about 50 ml., add 5 ml. of concentrated hydrochloric acid, and cool in iced water. Stir the solution thoroughly as it is cooling. When the bulk of the lead chloride has separated out, collect it in a filter-paper, and wash it rapidly with ice-cold, dilute hydrochloric acid. Dissolve the lead chloride, collecting the solution in an evaporating-dish, by washing the paper once or twice with boiling water and finally with a hot solution of ammonium acetate to which some acetic acid has been added. This solution should be added to the filtrate.

With the second method, to be used when copper is not to be determined, after the lead has been separated, dilute the solution to about 300 ml., add 2 grm. of tartaric acid as concentrated, clear solution, and make alkaline with sodium hydroxide. Add a further 2 grm. of sodium hydroxide. Pass a rapid stream of  $\text{H}_2\text{S}$  until all the copper and lead have been precipitated as sulphides, and then heat the contents of the beaker on a hotplate for one hour. Filter through paper, and wash the precipitate



with a clear 2 per cent. solution of sodium sulphide. Reject the filtrate and washings. The precipitate should contain no trace of tin and antimony, which should have remained in solution as thio-salts. Make a hole in the paper and wash the bulk of the precipitate into an evaporating-dish. Pour a few millilitres of nitric acid, followed by hot water and bromine water, along the top edge of the paper. Continue to wash with small volumes of hot water and bromine water in succession, until all the sulphides have been dissolved.

Add 15 ml. of concentrated sulphuric acid to the contents of the dish and evaporate the dense white fumes to expel all nitric acid. If necessary, cool, wash down the sides of the dish with a few millilitres of dilute sulphuric acid, and repeat the evaporation. Dilute the cooled solution with 100 ml. of water, heat it to boiling, and filter through paper, washing with cold, dilute sulphuric acid. Set aside the filtrate for the determination of copper. Dissolve the lead sulphate from the paper in hot ammonium acetate which has been acidified with acetic acid, and collect the solution in the evaporating-dish which already contains the bulk of the lead. Determine the lead in this solution gravimetrically as lead sulphate (p. 74) after the expulsion of the acetic acid; or gravimetrically (p. 74) or volumetrically (pp. 154 or 155) as chromate. If a chromate process is chosen, it is not necessary to expel the acetic acid, but it may be desirable to use only a portion of the solution. About 0.3 grm. and 0.15 grm. of lead are suitable for determination by the gravimetric and volumetric methods, respectively.

*Second Method.* For the determination of lead, when copper is not required. For the gravimetric method take that weight of the finely-divided alloy which contains about 0.3 grm. of lead; for the volumetric process take portions containing 0.15 grm., or one portion containing about 0.75 grm. In the last case, make up the final solution to 250 ml., and take 50 ml. for each titration. In any event, do not take more than 2 grm. of metal.

Heat the alloy in a beaker with 20 ml. of concentrated sulphuric acid until it has completely disintegrated, and until the lead sulphate is pure white in colour. Cool, but not below 60° C., and carefully add 50 ml. of water to the moving solution. Boil for five minutes, and then allow the lead sulphate to settle out from the hot liquid. When the solution has cleared, decant it through an unweighed Gooch crucible. Remove more of the tin and antimony from the lead sulphate by adding 10 ml. of concentrated sulphuric acid to the precipitate in the beaker, and by boiling for five minutes. Cool again, but not below 60° C., add 30 ml. of water to the moving solution, boil for a further five minutes, allow the lead sulphate to settle out as before, and again decant the liquid through the crucible. Wash the lead sulphate in the beaker twice with small volumes of dilute sulphuric acid. Extract the solids in the Gooch crucible and those in the beaker with a hot solution containing ammonium acetate and acetic acid. Unite the two solutions, filter if necessary, and determine the lead by a chromate process (see above under *First Method*).

**Copper.** The filtrate from the determination of lead by the first method should contain only copper sulphate in dilute sulphuric acid. The copper may be determined by any of the standard methods for that metal.

### Analysis of Bauxite

Bauxite consists of the oxides of aluminium, ferric iron and titanium, together with silica, small quantities of manganese, moisture, organic matter, etc.

**Moisture.** About 1 gram. of the sample, powdered to pass a 100-mesh sieve, is accurately weighed into a crucible, dried at  $105^{\circ}\text{C}$ . to obtain the hygroscopic moisture, and then heated slowly in a covered platinum crucible to a full red heat (at least  $1000^{\circ}\text{C}$ .). The cover is removed and the crucible is heated to a high temperature in a blast lamp. The loss in weight represents combined water and organic matter.

**Silica.** Fuse a mixture of about 1 gram. of the finely-powdered sample with 6 gram. of anhydrous sodium carbonate and 4 gram. of anhydrous potassium carbonate in a platinum crucible at a full red heat for at least thirty minutes.

Extract the melt with dilute hydrochloric acid, evaporate to dryness, bake at  $110^{\circ}\text{C}$ ., extract with  $\text{HCl}$ , and collect and wash the silica, which at this stage will be very impure. Either ignite it and weigh it in a platinum crucible and find its weight by removing it with sulphuric and sidue with  $\text{KHSO}_4$ , extracting with hot, the solution to the filtrate); or fuse the the latter case treat the melt with dilute sulphuric acid and, without removing any solid residue, evaporate the solution until dense white fumes appear. Cool. Dilute the solution, and again collect and weigh the silica, adding the washings to the first filtrate.

Make up the filtrate from the silica to a known volume, say 250 ml.

**Iron** is best determined by reduction with stannous chloride and titration with potassium dichromate. Take one-fifth of the solution and use standard solutions of approximately 0.025 N. concentration.

**Titanium.** The colorimetric method is recommended (p. 244), but it must be remembered that the colour of iron in solution interferes. Therefore either the concentration of iron in the titanium standard must be brought to the same as that in the solution under examination; or the iron colour must be bleached by the addition of phosphoric acid, which, in turn, will to some extent bleach the titanium colour. The latter method is described below.

The Separation of Iron from titanium may be effected in the presence of an alkaline solution pass in stage remain

Take a suitable volume, say 25 ml., of the filtrate from the silica in a colorimeter or Nessler tube, and about 25 ml. of water in a second tube.

Bring the sulphuric acid content of both tubes to 5 to 10 per cent. by volume. Run syrupy phosphoric acid 0.5 ml. at a time, but not more than 3 ml. in all, into the solution for analysis until it is substantially colourless, stirring after each addition of the acid. Make the phosphoric acid content of both tubes the same, and add 3 ml. of ten-volume hydrogen peroxide to each. Add a standard solution containing about 0.001 gm. of titanium per millilitre to the standard tube until the colours are nearly the same. Make the volumes of both solutions equal, and complete the titration. Traces of fluoride in either solution will so interfere with the result that it will be worthless.

The titanium can also be determined by reducing it with zinc in a Jones reductor (p. 148). The reduced solution is collected in a known volume of a standard solution of ferric alum, and the quantity of iron not reduced by the titanium is titrated with a standard solution of titanous chloride in an atmosphere of carbon dioxide, using ammonium thiocyanate as indicator. As the quantity of titanium to be determined will probably be small, the standard solutions used must be comparatively dilute.

**Aluminium.** Three methods are available :

(a) An aliquot portion of the solution is diluted four times and the  $\text{Fe}_2\text{O}_3 + \text{TiO}_2 + \text{Al}_2\text{O}_3$  precipitated with ammonia. This mixed precipitate is ignited and weighed. Since the iron and titanium percentages are known, the percentage of alumina can be calculated. If phosphorus is present, it must be determined separately (see p. 288), and a correction made for it. This is a poor method, since all the errors are thrown on the alumina result.

(b) The alumina is determined by difference. This is even less satisfactory.

(c) The iron and titanium are separated from the aluminium by using cupferron ( $\text{C}_6\text{H}_5\text{N}\cdot\text{NO}\cdot\text{ONH}_2$ ). This reagent forms insoluble compounds with iron, titanium, vanadium and tin, and enables these elements to be separated from aluminium, nickel, manganese, phosphorus, etc.

Take an aliquot portion of the solution and dilute to 200 ml. Add enough sulphuric acid to raise the acid content to 10 per cent., and cool the solution in ice. Precipitate the iron and titanium with cupferron by adding a fresh, cold, 6 per cent. solution of that compound to the cold solution, which is being vigorously stirred. When no further permanent precipitation takes place, add as an excess one-fifth of the volume of the cupferron reagent already added. Allow the precipitate to stand for ten minutes in the cold, and then filter through a small Buchner funnel. Wash with a 10 per cent. solution of sulphuric acid containing 0.2 gm. of cupferron in 100 ml. Reject the precipitate.

Evaporate the filtrate to about 50 ml. Add 20 ml. of concentrated nitric acid and continue the evaporation until white fumes of sulphuric acid appear, to oxidise the cupferron. Cool, dilute, and repeat the evaporation with an additional 20 ml. of the nitric acid. Cool and dilute the solution of the aluminium. Precipitate the hydroxide by adding ammonia in the presence of ammonium chloride. Ignite and weigh the alumina.

Any phosphorus present in the ore will be here precipitated as aluminium phosphate. A suitable correction must therefore be made [see (a) above], but, as the aluminium phosphate will contain only alumina,

the precipitate may be fused with pyrosulphate, the melt extracted with sulphuric acid and the phosphate determined as phosphomolybdate without further purification.

Calcium, Manganese and Magnesium are determined in the filtrate from the aluminium (c) above, or in a solution from which the iron, titanium and aluminium have been removed by the basic acetate separation (p. 300). If manganese is present, it can be precipitated by bromine in ammoniacal solution. The calcium is determined as oxalate (p. 70), and the magnesium as pyrophosphate (p. 76). See also p. 290.

### Analysis of Commercial Aluminium

The virgin commercial metal may contain the following impurities: carbon, silicon, manganese, sulphur, phosphorus, iron, copper, titanium, and sodium. These impurities are determined as is described below, and the methods given also apply to certain of these elements in aluminium alloys (see, however, pp. 297 to 299). The sample for analysis must be in the form of filings, turnings, or borings.

**Carbon.** The total carbon is determined in 2 grm. of *coarse* borings of the metal by dissolving away the aluminium and iron in 200 ml. of a solution containing 300 grm. of copper potassium chloride,  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ , per litre.

The contents of the beaker should be acidified with 10 ml. of concentrated hydrochloric acid and should be heated, but not above  $50^\circ \text{C}$ . A little ignited asbestos should be added to make the collection of the carbon easier. The carbon is ignited in oxygen as is described on p. 306. The chromic acid wash-bottle must be present in the train, and a tube containing pumice impregnated with anhydrous copper sulphate (p. 88) should also be in position to extract any hydrochloric acid which may have been introduced.

**Silicon.** Weigh out 1 grm. of the millings or turnings into a 400-ml. beaker and dissolve the metal in 35 ml. of an acid solution containing 5 parts of water, 2 parts of concentrated sulphuric acid, 1 part of concentrated nitric acid, and 1 part of concentrated hydrochloric acid by volume. When the metal has dissolved, rinse down the cover and evaporate to dense white fumes. Continue the fuming for fifteen minutes. Collect the silica from this residue and wash it as is described on p. 297. Then ignite the precipitate at about  $900^\circ \text{C}$ . for one hour.

fusion mixture.

Manganese and Phosphorus are determined in 5 grm. of the metal by the bismuthate method and the phosphomolybdate method, respectively,

as described for steel (pp. 311 and 310). Dissolve the aluminium initially in 50 per cent. sulphuric acid, or in aqua regia, respectively.

**Sulphur** is determined by dissolving 5 grm. of the metal in aqua regia, precipitating the resulting  $\text{H}_2\text{SO}_4$  as  $\text{BaSO}_4$ , and weighing the sulphur in this form (p. 65).

**Iron** is determined in the filtrate from the determination of silicon by the acid process, either by titration with standard permanganate after reduction with zinc, or by titanous chloride without reduction, or electrometrically (p. 216). The standard solutions used should be approximately 0.105 normal. For the determination of iron in the presence of titanium, see under "Titanium" (below).

**Copper** is determined in a 5-grm. sample, either electrolytically or by the iodide method. In the former case, dissolve the aluminium in 100 ml. of 50 per cent. sulphuric acid. When action has ceased, add 25 ml. of concentrated nitric acid, boil to expel oxides of nitrogen, filter into a beaker of suitable shape, and electrolyse (p. 230). For the iodide method, dissolve in 50 ml. of the sulphuric acid as above, add 5 ml. of nitric acid and evaporate to dense white fumes. Extract the residue with water, filter, and precipitate the copper in the filtrate with  $\text{H}_2\text{S}$ . Dissolve the copper sulphide in nitric acid, oxidise with bromine, and boil until the excess of this reagent has been expelled. Neutralise with sodium carbonate and acetic acid, and proceed as directed on p. 288.

**Titanium**, if present, will be collected in part with silica after dissolution of the metal in the acid mixture and fuming. After the silica precipitate has been ignited, treat it with hydrofluoric and sulphuric acids. Fuse the residue with a small quantity of potassium bisulphate, dissolve the melt in dilute sulphuric acid, and add this solution to the filtrate from the silica. Evaporate the whole to 100 ml., add 5 ml. of concentrated sulphuric acid and 3 grm. of iron-free zinc, and heat until the zinc is nearly dissolved. Filter, and determine the titanium in the solution colorimetrically (p. 244). The iron in the same solution is reduced a second time with zinc, and titrated with standard permanganate to obtain the iron plus the titanium.

**Sodium.** This determination is difficult; the aluminium is heated at  $900^\circ\text{C}$ ., and the sodium liberated is dissolved in water, and the alkaline solution titrated with acid.

Alloy	Al	Cu	Mg	Ni	Zn
Aluminium bronze . .	5-10	95-90	—	—	—
Alloy for castings . .	86-89	14-11	—	—	—
Alloy for light scientific instruments . .	75-80	—	25-20	—	—
Alloy for castings . .	82-86	4-2	—	—	14-12
Special strength alloys . .	91	4	1.5	2	—
Silicon alloy . .	86-90	—	—	—	10-14 Si

### Analysis of Aluminium Alloys

The percentage compositions of some typical aluminium alloys are summarised in the Table. They may also contain in addition small quantities of manganese, silicon, iron, and titanium. It is important, therefore, that the quantitative analysis be preceded by a qualitative examination of the alloy, and that the analytical scheme described below be modified to suit the particular case.

**Silicon.** The metal should be in the form of millings or very fine turnings. If the alloy has been made from aluminium of high purity, take 5 grm.; if it is an aluminium-silicon alloy, take 0.25 grm.; otherwise take 2 grm. Digest the portion with 30 ml. of a 10 per cent. solution of sodium hydroxide which has been freshly prepared. Use a covered, 200-ml., nickel crucible. When nearly all the aluminium has dissolved, wash down the sides of the crucible with a little hot water, replace the lid, and boil for ten minutes. Then dilute to about 50 ml. and boil until the residue is either in solution or in suspension.

Put 35 ml. of concentrated sulphuric acid and 35 ml. of water into a 400-ml. beaker, and stir the contents of the crucible into this solution. Wash out the crucible with a small volume of 50 per cent. sulphuric acid and then with water, and transfer all solid particles to the beaker, using a rubber-tipped glass rod. Evaporate the contents of the beaker on a hotplate until obvious white fumes appear, and continue the heating for fifteen minutes. Care must be taken to avoid loss by spitting. When the liquid is cold, dilute it to 200 ml. with hot water, break up the solid residue with a rubber-tipped glass rod, and then boil the solution gently until all soluble salts have dissolved (perhaps fifteen minutes). Collect the silica on filter-paper, using hot water to wash out the beaker, and then wash it three times with hot hydrochloric acid which has been diluted with three times its own volume of water. Finally, wash with hot water until the washings are free from chlorides. Dry the precipitate, and ignite it in a weighed platinum crucible at a high temperature, preferably using a muffle furnace. Determine the silica from the loss in weight of the precipitate after treatment with hydrofluoric and sulphuric acids (p. 100).

For another method, see p. 205.

*Note 1.* If the silicon content of the alloy is high and the treatment with

**Iron.** Dissolve 2 grm. of the alloy in 60 ml. of mixed acid solution (p. 295). Remove the silica by fuming and filtering, and determine the iron by one of the methods suggested for "Iron in Aluminium," p. 296; or determine the iron in a fresh sample potentiometrically (p. 216).

**Copper.** Dissolve 2 grm. of the fine drillings in 40 ml. of a 25 per cent. solution of sodium hydroxide in a beaker. When all action has ceased, dilute to 100 ml. with hot, air-free water. Filter, and wash with hot water. Dissolve the residue in 1 : 1  $\text{HNO}_3$  to which a few drops of concentrated  $\text{H}_2\text{SO}_4$  have been added, and heat to remove oxides of nitrogen. After the  $\text{P}_H$  has been suitably adjusted, determine the copper in this solution electrolytically or by the iodide method; or the alloy may be dissolved in acid and the copper determined as described on p. 296.

**Nickel** is best determined in a fresh sample, though the solution from which the copper has been removed by electrolysis or the solution in which the iron has been determined can be used. These solutions are evaporated down to about 50 ml., 3 grm. of tartaric acid or such greater quantity as may be required to prevent the precipitation of the iron and the aluminium are added, and the solution is made just alkaline with ammonia. The nickel is then precipitated with dimethylglyoxime (p. 62). If a fresh sample is used, take 2 grm. of the drillings, dissolve them in mixed acid (p. 295), remove the silica by fuming and filtering, and determine the nickel by the method indicated above.

**Magnesium.** Dissolve a suitable quantity of the alloy in 25 per cent. sodium hydroxide and collect and wash the residue, which will contain the magnesium, as is directed above under "Copper." Dissolve the residue in 10 ml. of hot, 50 per cent. hydrochloric acid, with the addition of a few drops of nitric acid if necessary. Dilute this solution to 100 ml., make it slightly alkaline with ammonia, and saturate it with  $\text{H}_2\text{S}$ . Allow it to stand for two hours in a warm place ( $40^\circ \text{C}.$ ), and then filter it, and wash the precipitate with water saturated with  $\text{H}_2\text{S}$  and containing 20 grm. of ammonium chloride and 20 ml. of dilute ammonia per litre. Acidify the filtrate with hydrochloric acid and remove all the  $\text{H}_2\text{S}$  by boiling. Then add 1 grm. of tartaric acid and determine the magnesium as magnesium pyrophosphate (p. 76).

**Zinc.** Take 1 grm. of the alloy if it is rich in zinc, or a proportionate quantity, and dissolve it in sodium hydroxide solution to which a little sodium carbonate has been added. After diluting, add a small quantity of alcohol to precipitate any colloidal ferric hydroxide. Filter and wash with hot, dilute sodium hydroxide solution. The filtrate will contain most of the zinc and the aluminium, but the residue will also probably contain some zinc. Therefore dissolve it in a small volume of hydrochloric acid to which a small crystal of potassium chlorate has been added, and boil to expel chlorine. Add sodium hydroxide until the liquid is strongly alkaline, filter, and add the filtrate to the main solution. To this, add 20 ml. of a 20 per cent. solution of sodium sulphide. Stir well, boil, and filter. Dissolve the zinc sulphide in hot, dilute hydrochloric acid, expel all  $\text{H}_2\text{S}$  by boiling, and then determine the zinc volumetrically by the

ferrocyanide method, using uranium acetate as external indicator (p. 199).

Alternatively, make the solution of zinc, after the removal of  $H_2S$ , nearly neutral. Add 10 grm. of ammonium chloride and 3 ml. of concentrated hydrochloric acid, and dilute to 200 ml. Heat to  $90^\circ C.$ , add 1 ml. of a solution containing 3 grm. of ferrous sulphate crystals per litre as indicator, and titrate with potassium ferrocyanide solution containing in addition 0.3 grm. of potassium ferricyanide per litre. At the end-point the colour of the solution changes abruptly from blue to green, but the addition of several more drops of the ferrocyanide reagent will change it to a cream colour.

The determination of zinc in aluminium alloys is not easy. It is therefore essential to run a blank in parallel with the assay. The blank can be either an aluminium alloy of known composition; or it can be made by weighing out suitable quantities of metallic aluminium and zinc (without melting them together), or by taking the appropriate salts.

### Analysis of Iron Ores

Iron commonly occurs as the oxides in the form of red and brown hematite and magnetite; as ferrous carbonate (spathic iron ore); and as clay ironstone, a mixture of carbonate and oxide with clay. Iron ores may contain the following constituents: moisture, carbon dioxide, silica, iron, titanium, aluminium, manganese, calcium, magnesium, phosphorus, and sulphur. Some ores also contain organic matter.

The analysis of titaniferous iron ores is described on p. 302, and the evaluation of chrome iron ore on p. 258.

**Moisture.** Since carbon dioxide and organic matter are usually present in the ore, the water must be determined by heating 2 grm. of the ore to dull redness, and absorbing the steam which is evolved in a weighed calcium chloride tube (p. 92).

**Carbon Dioxide** is determined by absorption (p. 85), using 2 grm. of the ore.

**Silica.** Weigh accurately from 5 to 10 grm. of the finely-powdered ore. Heat the ore gently with concentrated hydrochloric acid, add a little nitric acid, and continue the heating until it is judged that all soluble matter has been dissolved. Evaporate to dryness on a water-bath, and heat the residue at  $110^\circ C.$  in an air-bath. Make sure that all the nitric acid has been removed.

Treat the dry residue with concentrated hydrochloric acid. Then dilute the solution and heat it. Decant off the clear liquid through a filter. Treat the residue again with a small quantity of hydrochloric acid, heat, and filter the solution through the same filter into the same filtrate. Continue this treatment as long as any iron can be found by the ferrocyanide test in a drop of the acid last used. Wash and ignite the residue, and weigh it as silica and gangue. If necessary, the silica and gangue can be further examined by the methods described on p. 269. Transfer the filtrates and washings to a 500-ml. flask, and dilute to 500 ml. This solution is used for the following determinations.



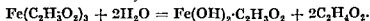
**Aluminium.** Add a ten-fold excess of disodium hydrogen phosphate to 50 or 100 ml. of the original solution, and dilute to 300 ml. Add 2 drops of methyl orange, and neutralise the solution with ammonium hydroxide. Add 10 ml. of dilute hydrochloric acid, 10 grm. of sodium thiosulphate crystals in solution, and 6 grm. of sodium acetate. The iron will be reduced and the bulk of the ferrous phosphate will not be precipitated. Boil until all traces of  $\text{SO}_2$  have been removed. Collect the precipitate of  $\text{AlPO}_4$  and wash it with a hot, 5 per cent. solution of ammonium nitrate. As this precipitate will probably contain iron phosphate, dissolve it in hot, dilute hydrochloric acid, and reprecipitate it as before, but using only 2 ml. of dilute  $\text{HCl}$  and 3 grm. of sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . Ignite the precipitate, and weigh it as  $\text{AlPO}_4$ .

**Iron.** Reduce the iron in 50 ml. of the original solution with stannous chloride, and titrate it with approximately decinormal potassium dichromate solution to obtain the total iron present. To determine the ferrous iron in the ore, digest a suitable weight of the sample with hydrochloric acid, using either the apparatus shown in Fig. 79, or that shown in Fig. 80 (p. 142), and titrate the solution at once with standard potassium dichromate.

**Manganese.** Dissolve 1 grm. of the finely-powdered sample in concentrated hydrochloric acid. Add a little hydrofluoric acid to aid the decomposition of the silicates, together with 10 ml. of concentrated sulphuric acid. Evaporate to dense white fumes and repeat the fuming, if necessary, to remove completely all traces of chlorine. Determine the manganese by the bismuthate method (p. 267), using standard potassium permanganate of approximately decinormal concentration.

**Calcium and Magnesium.** A suitable quantity of the original solution is taken, and, if the manganese is present in small quantity, the iron and aluminium are removed by the basic acetate method, and the manganese by bromine water and ammonia. If the percentage of manganese is high, it is removed with ammonium sulphide (p. 278). The calcium is determined as oxalate (pp. 70 and 158) and the magnesium as pyrophosphate (p. 76).

The basic acetate process, which depends on the fact that ferric, aluminium, or titanium acetate is hydrolysed in hot aqueous solutions to give a basic, insoluble salt, can be used to separate the above metals from nickel, cobalt, zinc and manganese, and from the alkali and alkaline earth metals :



Add dilute ammonia to the solution, which must be free from silica, until its colour is noticeably red, but no precipitate has formed. Then add a concentrated solution of ammonium carbonate, slowly at first and drop by drop at the end, until the precipitate produced dissolves very slowly. The solution, which will become very dark, must be stirred. If the end-point is overshoot, the solution may sometimes be brought to the right degree of acidity by adding a drop or two of hydrochloric acid, but more often it is better to add a considerable quantity of acid and to repeat the treatment with ammonia and ammonium carbonate.

Dilute the solution to 400 ml. with boiling water, and heat it to boiling.

A slight precipitate should form, but not before the temperature is higher than 70° C. Run in a boiling solution, some 25 ml. in volume, of sodium acetate. Use 3 grm. of the acetate, or 1 grm. for every decigram of iron and aluminium thought to be present, whichever quantity is the larger. Boil the solution for two minutes, not longer, after the acetate has been added.

Filter the hot solution at once through a *large, coarse* filter-paper held in a large funnel. Wash the precipitate twice with hot water containing 10 grm. of sodium acetate per litre, and allow it to drain thoroughly. Accelerated filtration should not be used, although it is an advantage to surround the funnel with a hot-water jacket (p. 54). The filtrate should be clear and colourless. As the precipitate will have retained some other metals, particularly manganese, it must be dissolved in hydrochloric acid and reprecipitated as above, the two filtrates being mixed. As the original basic-acetate precipitate will be contaminated with only a small quantity of manganese, it is not necessary to dissolve the whole of the iron and aluminium cleanly from the filter-paper for the reprecipitation, because the traces of manganese left in a small quantity of this precipitate will be negligible.

**Phosphate.** If arsenic has been found in the qualitative analysis, it must be removed by means of hydrogen sulphide before the phosphate is precipitated.

Digest 2 grm. of the ore with concentrated hydrochloric acid. If arsenic is present, remove it from the diluted solution, and then evaporate the filtrate to dryness. If arsenic is absent, evaporate directly to dryness.

Extract the residue with 25 ml. of water and 25 ml. of concentrated nitric acid, and add reagent potassium permanganate drop by drop until there is a permanent precipitate of manganese oxide. This completely removes any organic matter which may be present.

Clear the solution by adding a few drops of sulphurous acid, boil off the nitrous fumes, filter, and precipitate the phosphorus as ammonium phosphomolybdate. Determine the phosphorus in this precipitate either gravimetrically or volumetrically (pp. 78 and 202), or, for more accurate work, dissolve the phosphomolybdate in ammonia, and determine the phosphorus as magnesium pyrophosphate (p. 77).

For the determination of phosphorus in the presence of titanium, see p. 303.

**Sulphur.** Evaporate 50 ml. of the original solution nearly to dryness, so as to expel almost all the free acid. Precipitate the sulphate from the diluted solution with a little barium chloride solution. Allow the liquid to stand for several hours. Collect, ignite and weigh the  $\text{BaSO}_4$ .

**Copper, Arsenic and Antimony.** During the evaporation of the acid solution some of the arsenic will have volatilised. Therefore a fresh portion of the ore must be dissolved in some suitable solvent, and the solution treated with

d sulphides

The Composition of an Iron Ore is given in Table III., p. 491.

## Analysis of Titaniferous Iron Ores

**Silica.** When silica is determined in the usual way in ores containing titanium, a portion of the titanium is precipitated with the silica and the rest of the titanium remains in solution. In order to avoid this complication the ore should be decomposed by fusion with potassium bisulphate, but in this case a small quantity of silica will go into solution as potassium silicate when the mass is extracted with acid. The treatment of the ore for the determination of silica is therefore somewhat prolonged.

Reduce the ore to as fine a powder as possible in an agate mortar, and weigh accurately about 0.5 gm. of this powder into a large platinum crucible. Add 10 gm. of pure  $\text{KHSO}_4$ , cover the crucible carefully, and heat it over a small flame until the bisulphate is melted. The mass must be kept liquid and slight white fumes should be given off; the requisite temperature may be attained by maintaining the bottom of the crucible at a dull red heat. Take great care to regulate the heat in such a way as to prevent the melted bisulphate from frothing over the edge of the crucible. As soon as the ore is completely decomposed, remove the flame, take off the lid of the crucible and incline the crucible at an angle of about  $45^\circ$  so as to cause the fused mass to flow to one side of the vessel and to reach nearly to its edge.

When the crucible is cold, place it, together with the lid, in a basin, and treat the solid with concentrated sulphuric acid diluted with its own volume of water. Use about 30 ml. of the diluted acid, and note that if the acid concentration falls too low, the titanium sulphate will be hydrolysed. The melt may dissolve completely when the dish is heated. In this case, remove the crucible and lid, washing them down with hot water, and evaporate the solution to dense white fumes to dehydrate the silica. If there is a solid residue, decant as much as possible of the solution into a second basin. Add a few millilitres of water to the residue, and filter, collecting the solid on a filter-paper. Wash once with a little water, and collect the filtrate in the second basin. Dry and ignite the paper and residue, and fuse it with a little sodium carbonate as in the normal determination of silica in an insoluble silicate (p. 276). Extract with dilute hydrochloric acid, and transfer the solution and any residual solid to the second basin. Evaporate to dense white fumes. Cool. Dilute somewhat, and determine the silica by the ordinary method. The silicious residue must be fumed with hydrofluoric-sulphuric acid mixture, and the silica found by difference. Fuse any residue in the crucible with potassium bisulphate, extract with 1 : 1 sulphuric acid, and add the solution to the filtrate from the silica.

**Iron.** Dilute the filtrate from the silica to 200 ml., and saturate it with  $\text{H}_2\text{S}$ . Filter, and collect the filtrate in a flask fitted with two glass tubes, as in a wash-bottle. Pass  $\text{H}_2\text{S}$  through the tube which reaches to the bottom of the flask, until the liquid is again saturated with this gas. All the iron will now be reduced. Remove the  $\text{H}_2\text{S}$  by boiling the solution and by passing a current of  $\text{CO}_2$  through the flask. As soon as the issuing gases fail to turn lead acetate paper black, cool the flask, and titrate the iron, without giving it any opportunity to oxidise in the air, with standard potassium permanganate.

**Titanium.** Fuse 0.5 grm. of the very finely-powdered ore with potassium bisulphate, and extract the melt with 1 : 1 sulphuric acid. Heat until as much as possible of the solid is in solution. Then dilute to 250 ml., and pass the liquid and any suspended solid through a Jones reductor (p. 148), collecting the liquid in an excess of a solution of ferric sulphate. Titrate at once with titanous chloride (p. 189).

method for titanium.

In this case the mineral is fused with potassium pyrosulphate, the melt is extracted with dilute sulphuric acid, and any insoluble residue is re-fused and

precipitated as described  
precipitate is washed, dried

**Phosphorus.** Neutralise the spent liquid from the determination of the iron with ammonia, and reduce the iron by adding 50 ml. of a saturated solution of sulphur dioxide and boiling.

Precipitate the phosphorus as aluminium phosphate by adding an excess of aluminium sulphate and a slight excess of ammonia. Collect and wash the precipitate, which will be very impure, and fuse it with anhydrous sodium carbonate. Extract the melt with water and remove any precipitate of iron or titanium by filtration. Acidify the filtrate with hydrochloric acid, add a small excess of ferric chloride, and reprecipitate the phosphorus as ferric phosphate by again making the solution alkaline with ammonia. Filter and wash the precipitate. Dissolve it in nitric acid, and determine the phosphorus as ammonium phosphomolybdate (pp. 79 and 136).

### Analysis of Iron and Steel

Plain steel or ordinary cast iron will usually contain, in addition to the iron and carbon, appreciable quantities of sulphur, silicon, phosphorus and manganese. Traces of copper, arsenic and aluminium may also be present. Special steels and cast irons will also contain nickel or nickel and chromium. High-speed steel may contain chromium, tungsten, molybdenum and vanadium, while titanium is also a constituent of certain steels.

When determining the elements in steel or in other substances which are easy to weigh, it is sometimes useful to take a "factor quantity" of the material. The meaning of this expression is shown by the following example: In the determination of carbon in steel, the carbon is weighed as carbon dioxide (mol. wt. 44.01). If 0.4401 grm. of  $\text{CO}_2$  are collected, the steel sample must have contained 0.1201 grm. of carbon. That is, 10 milligrams of  $\text{CO}_2$  are obtained from 2.73 milligrams of carbon. If the steel contained 0.1 per cent. of carbon, 2.73 grm. of it would contain 2.73 milligrams of carbon and would give 10 milligrams of  $\text{CO}_2$ . In this case 10 milligrams of  $\text{CO}_2$  correspond with 0.1 per cent. of carbon. Thus,

if 2.73 gm. of steel are taken, the number of decigrams of carbon dioxide collected is the percentage of carbon in the steel; 2.73 (2.729) is, therefore, the "factor quantity" for carbon in steel.

The use of the "factor quantity" greatly simplifies final calculations, especially if a definite multiple or sub-multiple, say twice or one-third, of this quantity is analysed.

The sample for analysis should be in the form of fine turnings, drillings, or powder; and since cast iron and ferro-manganese contain greater quantities of impurities than do either wrought iron or steel, about three times as much wrought iron or steel is taken for analysis as is desirable in the case of cast iron.

**Total Carbon** (factor quantity, 2.729 gm.). The total carbon in iron and steel may be determined either by direct dry combustion, or by the combustion of the carbon after separation of the iron. The first method is more frequently used.

**Direct Dry Combustion of Carbon.** The steel is burnt in a stream of pure oxygen. The resulting gases are bubbled through a concentrated solution of chromic oxide, which oxidises any sulphur dioxide and retains it as sulphuric acid. The carbon dioxide is dried, if necessary, by passing it through a calcium-chloride tube and is collected in a weighed U-tube containing soda-lime.

The apparatus in order is as follows: The oxygen to be used is stored in an ordinary aspirator (the volume of each vessel of the aspirator should be about 10 litres), and the gas is first passed through a train of large U-tubes containing soda-lime and a bubbler containing concentrated sulphuric acid, to remove all traces of carbon dioxide, and to dry the gas. Alternatively, the oxygen straight from a cylinder may be passed through the train. In this case a safety bottle should be included between the cylinder and the first U-tube. This consists of a small bottle, about 7 cm. high and containing a layer of mercury about 2 cm. deep. The bottle is closed with a double-bored rubber bung. One of these holes is left open, whilst through the other passes the leg of a T-piece, the bottom of which can be adjusted to a suitable height below the surface of the mercury in the bottle. One of the arms of the T-piece is connected to the oxygen cylinder and the other, through a precision stop-cock for regulating the flow of gas, to the soda-lime train.

A suitable furnace for the combustion of steel must be available. It is unnecessary to describe such a furnace here, beyond saying that it is capable of giving a temperature of  $1,000^{\circ}\text{C}$ . and, preferably,  $1,350^{\circ}\text{C}$ . A temperature of  $1,350^{\circ}\text{C}$ . will be required if sulphur is to be determined by combustion. The combustion-tube should be about 12 inches in diameter. It should be of alundum, or of some material prepared specially for the purpose.

The sample is burnt in large boats of alundum or porcelain which are lined with a layer of alundum powder; this is prepared and sold for the purpose. After the combustion, the gases are passed through a layer of hot copper-oxide wire or of copper oxide made by

rolling up copper gauze and igniting it in the furnace. Care must be taken to prevent attack on the tube by splatterings of iron oxide and by the copper oxide. Vitreosil tubes and other tubes containing a high percentage of silica are particularly liable to crack if contaminated in this way, as the acid material of the tube reacts with the basic oxides.

The gases from the steel pass through a special Arnold bubbler containing a concentrated solution of chromic oxide either in 50 per cent. sulphuric acid or in concentrated sulphuric acid, and are dried by passage through a calcium chloride tube which has been so prepared that it does not absorb carbon dioxide (p. 88). If the chromic oxide has been dissolved in concentrated sulphuric acid, the calcium chloride tube is unnecessary, but a tube containing glass wool to trap spray must be substituted for it. The carbon dioxide is absorbed in a U-tube charged with soda-lime. This tube must be fitted with glass taps, and must be provided with a guard-tube to protect it from the air.

Heat the furnace, and ignite the boat and alundum powder in a stream of oxygen, the absorbent-tube being in the train and the oxygen passing through the Arnold bubbler at a rate of four to six bubbles a second. After ten minutes, or when it is judged that any carbon in the furnace has been "burnt out" and that all air in the absorbent-tube has been replaced by oxygen, disconnect this tube, close its taps, and leave it in the balance-case for exactly fifteen minutes. Then weigh it. Replace it in the train, pass the oxygen for a further ten minutes and repeat the cooling and weighing. Note that the tube is weighed only when it is filled with oxygen, and always with the taps closed, although one of these should be opened momentarily just before weighing to bring the pressure of the gas inside the tube to that of the atmosphere. If there is no substantial difference in the two weights, the determination of the carbon in the steel can be undertaken.

The metal must be freed from all traces of grease by washing it with ether and then with alcohol and drying it in a steam-oven. Withdraw the boat from the furnace and allow it to cool a little. Weigh out 2 grm., or the factor quantity, of the steel drillings (or a lesser quantity of cast iron), and pack them in the boat. The steel will burn better if it is closely packed, and advantage may be taken of this fact to control the combustion of a steel which tends to burn too vigorously. Push the boat into the centre of the hot combustion-tube. Close the tube at once, and pass oxygen at such a rate that four to six bubbles per second pass through the Arnold bubbler. When the steel burns, the oxygen will be absorbed rapidly, and the rate of flow of the gas from the reservoir may be increased for a short time. The aim should be to keep the gas passing through the bubbler at a constant rate. When the steel has been oxidised, continue to pass the oxygen for a further fifteen minutes; then disconnect the absorbent-tube, close the taps, and cool and weigh the tube under the standard conditions. A common source of error is in the weighing of the tube. The area of glass is comparatively large, and the quantity of moisture absorbed on it will vary appreciably if the conditions under which the tube is weighed are varied.

The occasional checking of the apparatus and method by carrying out the combustion of a steel of known carbon content is strongly advised. Standard steels can now be purchased. The beginner should obtain one

of these and practise with it until he has acquired the necessary technique, because the determination of carbon in steel by this method is satisfactory only in the hands of experienced workers.

any  
N

bary  
filtration, and the excess of baryta determined by titration with standard acid, using methyl orange as indicator. Alternatively, the excess of baryta may be titrated in the presence of the barium carbonate with dilute standard acid, using phenolphthalein (p. 185). These methods are little used.

**Combustion of the Carbon after the Removal of the Iron.** The powder or borings of the metal are digested with an excess of cupric ammonium chloride solution. The iron is dissolved and an equivalent weight of copper is at first precipitated, but, if the digestion is continued, the copper is redissolved and a residue only of carbon is left. The carbon is introduced into a small boat and ignited in a combustion-tube in a current of oxygen, and the carbon dioxide produced is absorbed by soda-lime, and is weighed. The process is used to determine carbon in cast iron.

**Preparation of the Cupric Ammonium Chloride Solution.** Dissolve 400 gm. of cuprammonium chloride,  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ , in water to which 50 ml. of concentrated HCl have been added, and make up the solution to 1 litre. Filter before use.

**Procedure.** Weigh out accurately 1 gm. of cast iron, or 5 gm. of wrought iron or steel, and digest the metal in the cold with from 100 to 200 ml. of the above solution. Stir occasionally with a glass rod to assist the disintegration of the metal. When most of the iron has dissolved, continue the digestion of the residual carbon and metallic copper at  $70^\circ \text{C}$ ., adding more of the copper solution if necessary until most of the copper has dissolved. As soon as the residue loses its red colour, collect the carbon upon an asbestos filter, having previously removed any scum of basic ferric chloride from the surface of the liquid by the addition of a little hot, dilute hydrochloric acid.

The iron from a number of samples can be dissolved conveniently at one and the same time by placing the weighed quantities of metal in the solvent in conical flasks arranged in series. The liquids are stirred by pulling air through the flasks, using a water-pump. If another conical flask containing a little mercury, to act as a trap, is placed between the pump and the reaction-vessels, the water can be left running over night. The next morning it will be found that the iron has gone into solution and that most of the copper has redissolved. The removal of the residual copper may then be hastened by heating the flasks gently.

asbestos fibres pass away in the liquid.  
a plug  
broken  
ryer of  
s used,  
as any

A special funnel may be made for the purpose of the filtration in the following way: A piece of combustion tube, about 10 cm. long and 1 cm. in internal diameter, is drawn out at one end until a small orifice only is left (Fig. 105). It will be found convenient to introduce a coiled piece of stout platinum wire into the funnel to be used for pushing out the asbestos into the boat when the filtration has been completed. The glass wool and asbestos are then introduced into the filter-tube above the wire coil, and are washed as is described above.

If a small platinum filter-tube is used instead of the glass tube, it may be pushed with its contents into the combustion-tube: the removal of the asbestos and carbon from the funnel thus becomes unnecessary.

An ordinary Gooch crucible may be used instead of a special filter-tube.



FIG. 105.

CARBON FILTER

The carbon is washed on the filter until it is free from chloride. The filter is then dried in a steam-oven, the asbestos containing the carbon is transferred to a porcelain or platinum boat, and the combustion is carried out in the manner described above for the direct dry combustion of steel. It is, however, advisable to include in the train a tube containing pumice impregnated with anhydrous copper sulphate (p. 88) to ensure that no hydrochloric acid passes into the potash bulbs. Alternatively, a coil of silver gauze may be placed between the copper oxide and the outlet tube. The silver will also remove any chlorine which may result from the inefficient washing of the filtered carbon. The separated carbon can be burnt at a considerably lower temperature than that necessary for the successful combustion of steel, but, as in the case of the direct dry combustion, the running of a blank is essential.

**Graphite.** Weigh out 5 grm. of steel, 1 grm. of grey, or 3 grm. of white, cast iron. Use coarse drillings. Heat them gently with nitric acid of sp. gr. 1.2, using 25 ml. of the acid per gramme of metal. As soon as the flocks of carbonaceous matter have disappeared, collect the insoluble residue of impure carbon on an asbestos filter, and wash it successively with hot water, a very dilute solution of potassium hydroxide, alcohol, ether, and again with alcohol. Dry the residue, and determine the amount of graphite in it by burning it in a stream of oxygen and absorbing and weighing the carbon dioxide.

**Combined Carbon in Steel, Wrought and Cast Iron by Eggertz's Method.** This colorimetric method is described on p. 217.

**Sulphur.** Two methods are in common use:

1. The sulphur is first evolved as hydrogen sulphide and this is collected and determined volumetrically. This process applies to plain steel; sulphur may be lost from cast iron or alloy steels.

2. The sulphur is converted into sulphuric acid, which is precipitated and weighed as barium sulphate. This method gives more accurate results than the first, and is of general application.

**Determination of Sulphur by Conversion into Hydrogen Sulphide** (1.603 grm. of steel containing 0.1 per cent. of sulphur requires 1 ml. of 0.1 N. iodine). Fit into the neck of a 200-ml. conical flask a doubly-perforated rubber stopper, which has previously been boiled with sodium



hydroxide solution to extract the sulphur. Through one hole in this stopper push a thistle funnel, which must nearly touch the bottom of the flask. The thistle funnel must be fitted with a tap. Into the other hole fit a delivery-tube which just passes through the bung, and which is bent twice; *once, near the end, at 140° and once at 40° to bring it vertical again.* The distance between the two bends should be about 20 cm.; this portion of the tube will act as a condenser. Connect the other end of the delivery-tube to a length of glass tubing which carries a bulb to prevent "sucking back," and which passes through a two-holed rubber stopper into a second conical flask. This tube should reach nearly to the bottom of the flask, and the flask should also be connected to a bulbed U-tube as a guard-tube. All stoppers and rubber tubing used as connecting pieces must previously have been boiled with sodium hydroxide solution to extract any sulphur they contained.

Dissolve 5 gm. of cadmium chloride in 200 ml. of 0.880 ammonia and dilute to 1 litre. Place about 80 ml. of this solution in the second conical flask and also a few millilitres of it in the guard-tube.

Weigh out accurately from 5 to 10 gm. of the steel or wrought iron into the first flask, and displace all air by passing a current of hydrogen, *via* the thistle funnel, through the apparatus. The hydrogen must be cleaned by passing it first through a solution of lead nitrate in sodium hydroxide and then through the water, before it is allowed to enter the flask. Disconnect the lead from the hydrogen apparatus from the thistle funnel, and dissolve the steel in 50 ml. of concentrated hydrochloric acid which has been diluted with 20 ml. of water. With some steels the action will be brisk, and it may be necessary to add the acid from the thistle funnel in small quantities at a time and to cool the flask. When the evolution of gas has almost ceased, heat the flask gently with a small flame until the metal has dissolved, and then boil it gently for ten minutes, passing a slow stream of the pure hydrogen through the apparatus. Then remove the flame, but continue to pass the hydrogen for a further ten minutes. The sulphur will be converted into hydrogen sulphide and will be carried away in the stream of hydrogen and steam. It will be precipitated by the cadmium solution as impure cadmium sulphide.

Filter the precipitate, and return it, together with the paper, to the flask which originally contained the cadmium. (Neither precipitate nor flask should be washed.) Add about 100 ml. of water and 20 ml. of dilute hydrochloric acid. Oxidise the  $H_2S$  immediately with an excess of a standard, approximately 0.05 N. solution of iodine (10 ml. is usually sufficient), and titrate the excess of iodine with 0.05 N. sodium thiosulphate, using starch as indicator.



*Note 1.* Alternatively, flush out the apparatus with carbon dioxide instead of with hydrogen. If carbon dioxide is used, the  $H_2S$  must be collected in a solution containing 25 gm. of cadmium acetate and 20 ml. of glacial acetic acid per litre instead of in the ammoniacal cadmium solution. The latter would lead to the formation of ammonium carbonate.

completed and the excess of the oxidant is expelled by boiling the liquid, and the sulphur is precipitated and determined as  $BaSO_4$ .

*Determination of Sulphur as BaSO<sub>4</sub>* (1.373 gm. of steel containing 0.01 per cent. of sulphur gives 1 milligram of BaSO<sub>4</sub>). Dissolve 5 gm. of steel, or 2 gm. of cast iron, in 50 ml. of nitric acid. Use an evaporating-dish. If solution is slow, it may be hastened by adding from time to time a few drops of hydrochloric acid. When the iron is in solution, add 0.5 gm. of sodium carbonate to fix the H<sub>2</sub>SO<sub>4</sub>, evaporate to dryness at a moderate heat on an iron plate or air-bath, and bake gently. Cool, add 30 ml. of concentrated hydrochloric acid, and repeat the evaporation and baking. Extract the residue with a further 30 ml. of concentrated hydrochloric acid, and evaporate until the solution is syrupy. Then add 5 ml. of hydrochloric acid and 5 gm. of fine zinc granules. These must be added cautiously, and their purpose is to reduce the iron to the ferrous state and so prevent precipitation of iron with the precipitate of barium sulphate. Heat the dish on a water-bath until the iron has been reduced and the evolution of hydrogen has ceased, and then filter. Wash the residue with water containing about 2 ml. of hydrochloric acid per 100 ml. Boil the filtrate and runnings, and to the boiling liquid add 10 ml. of hot reagent barium chloride (see p. 517) in excess. After standing for two hours, or, better, overnight, filter through an ashless paper, wash with hot, dilute HCl and then with hot water, and dry, ignite and weigh the BaSO<sub>4</sub> (p. 65).

This method gives the more accurate results, provided care is taken to remove the free nitric acid, to keep the volume of the liquid small, and to add a fair excess of barium chloride solution.

for.

*Silicon* (4.695 gm. of steel containing 1 per cent. of silicon give 0.1 gm. of SiO<sub>2</sub>). Dissolve 2 gm. of cast iron, or 5 gm. of steel or wrought iron, in 80 ml. of a solution containing 10 ml. of concentrated sulphuric acid, 15 ml. of concentrated nitric acid and 55 ml. of water. Use a covered evaporating dish, and take care to prevent loss by spirting if the action is violent. When the metal has dissolved, evaporate until dense white fumes of sulphuric acid are evolved. All organic matter must be removed and the silica must be dehydrated thoroughly. Allow the contents of the dish to cool, and add about 100 ml. of water and 5 ml. of concentrated hydrochloric acid. Dissolve the salts as rapidly as possible by heating and stirring, and then at once filter through paper. Wash the precipitate with cold, 5 per cent. hydrochloric acid until the filtrate fails to give a

reaction for iron, and then with hot water until it is free from acid. Then dry the precipitate, ignite it in a platinum crucible and weigh it.

Since the silica may contain impurities, it is best to ascertain the weight of pure silica present by treating the weighed substance with pure hydrofluoric acid and a little concentrated sulphuric acid (p. 101).

Phosphorus (1.35 grm. of steel containing 0.1 per cent. of phosphorus requires 1 ml. of normal alkali). The phosphorus is converted into phosphate by the action of concentrated nitric acid, and is then precipitated as phosphomolybdate (a); or the phosphomolybdate is converted into lead molybdate and weighed as such (b). This method has the great advantage that the precipitate weighed represents a very much smaller weight of phosphorus; about 7 milligrams of phosphorus yield 1 grm. of precipitate.

(a) *Determination as Phosphomolybdate.* Dissolve 2 grm. of the steel in 100 ml. of dilute nitric acid (one volume of acid and two of water), using a beaker if the phosphorus is subsequently to be determined by a gravimetric process. Otherwise use a conical flask. When all the steel has dissolved and most of the oxides of nitrogen have disappeared, add 5 ml. of reagent potassium permanganate solution (p. 518), and boil for three minutes to oxidise the phosphorus completely and to remove any carbides. If no precipitate has appeared, add more of the permanganate and continue to boil. Dissolve the precipitate which is obtained finally by the addition of a solution of sulphur dioxide, which must be added slowly, drop by drop, in only slight excess. The solution should meanwhile be boiled, and the boiling should be continued for two minutes after the disappearance of the manganese dioxide. If a precipitate of silica or tungstic oxide is now present, filter.

To the solution, cooled to 35° C., add 50 ml. of ammonium molybdate reagent (p. 70). Shake or stir the solution for five minutes and allow it to stand at 35° C. for fifteen to thirty minutes. The precipitate may be collected in a Gooch crucible, washed with 1 per cent. nitric acid, and weighed as  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , after drying it at 110° C. (p. 78.); or it may be collected in an ordinary filter-paper, washed with 1 per cent. potassium nitrate, and determined volumetrically (p. 136), the precipitate and paper being returned to the original flask. Solutions of acid and alkali of 0.05 N. concentration are usually suitable.

Alternatively, the phosphomolybdate may be converted into magnesium pyrophosphate (p. 77). Dissolve the yellow precipitate in ammonia, and pour a solution containing 0.5 grm. of citric acid, 10 ml. of concentrated hydrochloric acid and 15 ml. of water over the paper to dissolve any traces of ferric phosphate which may be present.

(b) *Determination by Weighing as Lead Molybdate ( $\text{PbMoO}_4$ )* (7.04 grm. of steel containing 0.1 per cent. of phosphorus give 1 grm. of  $\text{PbMoO}_4$ ). Wash the precipitate of phosphomolybdate six times with 1 per cent. nitric acid, and then dissolve it by pouring on to it 4 ml. of concentrated ammonia. Wash the solution out of the filter-paper or Gooch crucible with hot water and acidify it with hydrochloric acid. Then add 10 ml. of a 4 per cent. solution of lead acetate and heat to boiling. Finally, add a boiling solution containing 10 grm. of ammonium chloride and 10 grm. of ammonium acetate in 100 ml. of water. Collect the precipitate, as

soon as it has settled, in a Gooch or alundum crucible, wash it with hot water and weigh it after ignition over a Bunsen burner to constant weight, at not more than a good red heat.

**Manganese** (1.099 grm. of steel containing 0.1 per cent. of manganese requires 2 ml. of 0.05 N.  $\text{KMnO}_4$ ). Manganese in iron and steel is usually determined by the bismuthate process (p. 267).

About 1 grm. of the steel is dissolved by heating with 35 ml. of  $\text{HNO}_3$  (sp. gr. 1.2). After the action of the acid has been completed, oxidise the organic matter present in the solution by gradually adding sodium bismuthate until the pink colour of the permanganic acid either persists or becomes changed to brown manganic oxide when the liquid is boiled: this may require about 0.5 grm. of the bismuthate. Then gradually add either sulphurous acid or ferrous sulphate until the liquid is clear, heat to remove most of the nitrous fumes, cool and proceed as described on p. 267. Solutions of approximately 0.05 N. concentration are convenient.

*Note.* Cobalt interferes with this method, and, if present, must be removed. Chromium is oxidised by sodium bismuthate when the solution is hot, and care must be taken to ensure that any chromic acid produced in the preliminary oxidation is reduced by the  $\text{SO}_2$  or ferrous sulphate. The amount of chromium

The carbides in cast iron may be somewhat difficult to oxidise. Use 1 to 2 grm. of bismuthate in the preliminary oxidation and boil vigorously.

**Colorimetric Determination of Manganese in Iron and Steel.** The steel is dissolved in nitric acid and the manganese is oxidised by periodate or by ammonium persulphate in the presence of silver nitrate (p. 241).

**Copper** (6.35 grm. of steel containing 0.1 per cent. of copper require 1 ml. of 0.1 N. sodium thiosulphate). Dissolve 10 grm. of a plain carbon steel, or a suitable quantity of a cupro-steel, in 20 ml. of  $\text{H}_2\text{SO}_4$  diluted with 80 ml. of water. Heat until the iron is dissolved and then dilute to 300 ml. The copper will now probably be partly in solution and partly undissolved. Precipitate the soluble copper by adding 1 grm. of copper-free zinc and by stirring until nearly all the zinc has been dissolved. Filter through a Gooch crucible or coarse paper, working rapidly to avoid oxidation of the copper. Then dissolve the precipitate in 3 or 4 ml. of concentrated nitric acid, and boil to remove oxides of nitrogen.

The copper in this solution may be determined iodometrically (p. 177), by electrolysis (p. 228), or colorimetrically, using the diethyldithiocarbamate method (p. 239). Iron and zinc interfere with the colorimetric method, but not if the solution is strongly ammoniacal and the citrate radical is present (p. 240). Although the interference of iron in the iodometric method is minimised by the addition of potassium fluoride, it is better when using either this or the electrolytic method, to remove the iron from the solution of copper in nitric acid by making the liquid strongly alkaline with ammonia, by filtering off the precipitate of ferric hydroxide and washing it with dilute ammonia. If this precipitate is at all large, it must be dissolved in hydrochloric acid and reprecipitated.

Copper may also be separated from iron by the ether separation (see below under "Nickel").

**Aluminium** (2.2 gramm. of steel containing 0.1 per cent. of aluminium give 10 milligrams  $\text{AlPO}_4$ ). The aluminium is precipitated as phosphate under conditions which preclude the precipitation of iron.

Dissolve 10 gramm. of the steel in 60 ml. of hot 50 per cent.  $\text{HCl}$  and filter the solution. Determine the aluminium as described on p. 300. Use 2 gramm. of disodium hydrogen phosphate crystals for the precipitation. The first precipitate will probably be contaminated with silica, and therefore dissolve it on the paper with the hot, dilute hydrochloric acid so that the silica will be left behind.

Copper, titanium and chromium interfere. Copper must first be removed with  $\text{H}_2\text{S}$ . Titanium is weighed as titanium phosphate with the aluminium, and an allowance for it must be made by determining it separately (p. 316). Chromium must be removed by converting it to chromate by fusing the second phosphate precipitate with sodium carbonate and potassium nitrate, dissolving the melt in hydrochloric acid, and reprecipitating the phosphate again, this time without the addition of sodium thiosulphate.

**Nickel** (2.032 gramm. of steel containing 1 per cent. of nickel give 0.1 gramm. of  $\text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4$ ). Nickel in steel is nearly always precipitated as nickel dimethylglyoxime (p. 62) and weighed as such. The nickel is first separated from the iron (a) by shaking a solution of the chlorides with ether, in which ferric chloride is soluble; or (b) the nickel is precipitated from a solution containing tartrates, in which the iron is soluble.

(a) *Separation with Ether.* Dissolve 2 gramm. of the steel in dilute  $\text{HCl}$  of 1.1 specific gravity, add sufficient  $\text{HNO}_3$  to convert the iron into the ferric state, and remove the nitrous fumes by boiling. Make sure by testing with a freshly-made solution of potassium ferricyanide that all the iron has been oxidised. Evaporate the solution until the  $\text{FeCl}_3$  begins to form a skin upon the surface of the liquid. Add diluted  $\text{HCl}$  of 1.1 specific gravity in order to redissolve any basic salt, and transfer the liquid to a stoppered separating-funnel of 250 ml. capacity. Rinse out the solution into the funnel with successive small portions of the dilute hydrochloric acid, taking care that the whole volume of the liquid does not exceed 50 ml., and then add 12 ml. of concentrated hydrochloric acid to the contents of the funnel.

Now pour 40 ml. of ether into the funnel and shake the liquids together for about eight minutes. If the solution is warm, the stopper of the separating-funnel may be blown out. The ether will remove the  $\text{FeCl}_3$  from the solution, and will form an emerald-green layer above the aqueous solution. Let the funnel stand for a few minutes and then transfer the acid aqueous solution, containing the nickel chloride, to another separating-funnel containing 40 ml. of ether. Shake the ether in the first funnel with a little of the dilute  $\text{HCl}$  and allow the lower layer to flow into the second funnel. Repeat the washing with fresh acid, and finally pour off the green, ethereal solution from the first funnel into a residue bottle for the recovery of the ether. Shake the contents of the second funnel for ten minutes to remove the last trace of the ferric chloride from the acid liquid. Then allow the acid liquid to flow into an evaporating-basin, and wash out the last portions with the dilute acid as before.

The solution of the nickel chloride will contain a little ether which must be removed by boiling. Sometimes the ether used contains a reducing agent, and it is therefore advisable to test the solution of nickel chloride for the presence of ferrous iron. If ferrous iron is present, it must be oxidised by boiling the solution with nitric acid. If the steel contains chromium or all the iron has not been removed, add 1 grm. of tartaric acid, make the solution slightly alkaline with ammonia, and determine the nickel as dimethylglyoxime (p. 62). If copper is present in the steel it will be in the nickel fraction, from which it may be separated by precipitation with hydrogen sulphide, if it is necessary to determine it. Copper, except in large quantity, does not interfere with the glyoxime method.

The nickel may also be determined volumetrically by the cyanide process (p. 106), provided copper, manganese, and other interfering elements are absent.

(b) *Without Separation.* Dissolve and oxidise the steel as for the other separation. Then dilute the solution to 300 ml. and add 3 grm. of tartaric acid per gramme of steel. Make just alkaline with ammonia, warm, and add the dimethylglyoxime. If this method is used it is most important to convert all the iron to the ferric state.

Chromium (1.734 grm. of steel containing 0.1 per cent. of chromium is equivalent to 1 ml. of 0.1 N.  $K_2Cr_2O_7$  or  $KMnO_4$ ). The steel is dissolved in acid and the chromium is oxidised by potassium permanganate to chromic acid. The completion of this oxidation is indicated by the appearance of a turbidity, which is due to the precipitation of manganese dioxide by the interaction of manganous sulphate with the excess of permanganate. The precipitate is removed by filtration and a measured volume of standard ferrous solution is then added in quantity more than sufficient to reduce the chromic acid, and the excess is titrated with standard potassium dichromate solution.

**Procedure.** Dissolve 2 gram. of the steel in 20 ml. of 20 per cent sulphuric acid (one volume of concentrated acid and three volumes of water). Boil the acid until solution is nearly complete; then continue the boiling after adding 2 or 3 ml. of concentrated nitric acid to oxidize the iron. When the oxides of nitrogen have been expelled, dilute to 200 ml. with hot water. Then run approximately 0.1 N. potassium permanganate (3 c.c.) into that hot solution, until a turbidity persists, and add 0.1 N.

permanganate in excess. Boil for ten minutes to convert the excess of permanganate into manganese dioxide, filter through asbestos in a Gooch crucible, add a known volume in excess of decinormal ferrous ammonium sulphate solution, and determine the excess of the ferrous sulphate by titration with standard dichromate solution, using potassium ferrieyanide as external indicator; or, titrate with the standard ferrous solution, using ferrous phenanthroline as internal indicator (p. 145).

Instead of removing the manganese dioxide by filtration, it may be reduced by the addition of hydrochloric acid. Add 80 ml. of dilute acid, and boil until the chlorine has been expelled. Half the volume of the solution may have to be removed before this result is obtained.

Chromium may also be determined potentiometrically (p. 217).

Another method for the oxidation of the metal is described on p. 217; and a method for chromium in the presence of vanadium on p. 218.

**Tungsten** (0.793 grm. of steel containing 0.1 per cent. of tungsten gives 1 milligram of  $WO_3$ ). The steel is dissolved in hydrochloric or nitric acid, or in aqua regia. The solution is evaporated to dryness, and extracted with hydrochloric acid, when a residue of silica and tungstic oxide,  $WO_3$ , will remain. The silica is removed from this residue by means of hydrofluoric and sulphuric acids, and the tungstic oxide is weighed.

Digest 2 grm. of the fine steel drillings with 50 ml. of concentrated hydrochloric acid at a temperature just below the boiling-point, adding a few drops of concentrated nitric acid from time to time, until a clear solution is obtained and all the iron is in the ferric state. The nitric acid is only added as an oxidant, and should be used sparingly. Evaporate the solution until a pasty mass results, and then add 100 ml. of water and 10 ml. of hydrochloric acid, and boil gently for a few minutes. Add 5 ml. of a solution of cinchonine hydrochloride (made by dissolving 10 grm. of the alkaloid in 25 per cent. hydrochloric acid and diluting to 100 ml. with the dilute hydrochloric acid), and set the beaker aside for half an hour on a hotplate. Its contents should not boil. The cinchonine hydrochloride will precipitate any tungsten which may be in solution. Collect the precipitate on a filter-paper, and wash it with a solution containing 3 ml. of the above cinchonine solution and 3 ml. of concentrated hydrochloric acid per 100 ml., and, finally, once with water; the last acid filtrate should contain no iron. Dry the precipitate and ignite it in a platinum crucible, but do not exceed  $850^\circ\text{C}$ . This precipitate will be contaminated with silica and, possibly, with iron. Remove the silica by treatment with hydrofluoric and sulphuric acids (p. 100). Then fuse the residue with sodium carbonate, extract with water, and filter. Any iron will then be in the precipitate. Precipitate the tungstic oxide from the filtrate by hydrochloric acid, using the above method, and collect, ignite in a muffle furnace at  $800^\circ\text{C}$ . and weigh it.

**Molybdenum** (2.615 grm. of steel containing 1 per cent. of molybdenum give 0.1 grm. of  $PbMoO_4$ ). The method consists in preparing a solution of the steel by heating it with hydrochloric acid, nitric acid being added as an oxidant in small quantities only. The iron and manganese are precipitated from this solution by adding sodium hydroxide in excess. The Mo is precipitated from the filtrate as lead molybdate,  $PbMoO_4$ , in the presence of acetic acid, and weighed as such.

Treat 2 gm. of the drillings as recommended under "Tungsten" (above), but extract the pasty mass by heating it gently with 25 ml. of water and 10 ml. of hydrochloric acid. If tungsten is present, the residue will be yellow and the solution must be filtered. Reduce the acidity of the filtrate by the careful addition of sodium hydroxide solution of reagent concentration (p. 517), but stop adding the alkali before the colour of the solution turns red. Place 15 ml. of the sodium hydroxide, or a proportionate quantity if a weight other than 2 gm. of the steel has been taken, in a beaker, dilute to about 100 ml. and heat to the boiling-point. Run the hot solution of the molybdenum slowly into this solution, stirring vigorously all the while. All the molybdenum should remain in solution and all the iron and manganese should be precipitated. Make up the cold liquid, without filtering, to 500 ml. Allow the precipitate to settle and then filter, collecting 250 ml. of the filtrate, corresponding with 1 gm. of the steel, for the determination. To this portion add a drop of methyl orange as an indicator, and then run in hydrochloric acid in definite excess. Boil the solution and slowly add lead acetate solution, made by dissolving 40 gm. of the crystals in water containing a little acetic acid and enough ammonium acetate to convert the hydrochloric acid in the molybdenum solution to acetic acid, and diluting to 1 litre. Ten ml. of this solution will precipitate 10 milligram of molybdenum; 5 to 10 per cent. of it should be added in excess.

Allow the precipitate to settle, collect it in a Gooch crucible or filter-paper, and wash it with hot water. Ignite the lead molybdate at a red heat to constant weight. If the temperature is not allowed to rise too high, no special care need be taken in igniting the precipitate apart from the filter-paper, if the latter has been used.

Vanadium and tungsten interfere, but the molybdenum may be separated from the vanadium by the ether process (p. 312).

*An alternative and shorter method* now widely used in steel analysis is to precipitate the molybdenum with "cupron" ( $\alpha$ -benzoin oxime). Silica and copper chromates must be reduced by passing  $\text{SO}_2$ .

1 gm. of hexavalent Mo in 200 ml. of 5 per cent. solution of cupron, with 50 ml. of 10 per cent. sodium hydroxide solution, and weighed as  $\text{MoO}_3$ .

Vanadium (5.095 gm. of steel containing 0.1 per cent. of vanadium are equivalent to 1 ml. of 0.1 N.  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{KMnO}_4$ ). The process depends on the determination of the amount of oxygen required for the conversion of  $\text{V}_2\text{O}_4$  into  $\text{V}_2\text{O}_5$ .

Dissolve 2 gm. of the drillings in dilute sulphuric acid, and proceed exactly as for chromium (p. 313) by removal of the manganese dioxide by filtration, but titrate the excess of ferrous sulphate with standard, approximately 0.1 N. potassium permanganate. The ferrous salt reduces the vanadic acid and the chromic acid, and the permanganate oxidises the excess of the ferrous salt and the  $\text{V}_2\text{O}_4$  once again to  $\text{V}_2\text{O}_5$ . From this experiment the quantity of chromium present may be calculated.



Again reduce the  $V_2O_5$  with a known quantity of ferrous ammonium sulphate and titrate this excess either with potassium permanganate or potassium dichromate, using potassium ferricyanide as external indicator. When the indicator no longer reacts with a large drop of the solution, the iron has been oxidised. As the iron is oxidised before the vanadium, the quantity of vanadium present can be determined.

The determination of vanadium alone or in the presence of chromium by the electrometric method has been described on p. 218.

**Titanium.** Dissolve 5 gramm. of the steel in 30 ml. of concentrated hydrochloric acid. If there is an apparent residue, separate it and ignite it in a platinum crucible. Set the crucible aside.

Dilute the main solution to 200 ml. and add ammonia until there is a faint permanent precipitate. Just clear this with dilute hydrochloric acid, add 10 gramm. of sodium thiosulphate in concentrated solution, and boil for twenty minutes. The titanium will be precipitated as  $TiO_2$ , but this precipitate will be impure. Filter through paper and wash with very dilute acetic acid. Dry the precipitate and the paper, and ignite them in the platinum crucible which already contains some of the titanium.

Fuse the contents of the crucible with sodium carbonate, and extract the cooked melt with water. The solution should contain no titanium. Collect the solid residue on a filter-paper, wash it with hot water, dry it, and again ignite it in the platinum crucible. The residue may be weighed as  $TiO_2$  at this stage, but it may still be impure. For a more accurate result, particularly if the quantity of oxide is small, fuse it with potassium bisulphate, dissolve the melt in hot sulphuric acid which has been diluted with its own volume of water, and determine the titanium colorimetrically with hydrogen peroxide (p. 244).

If the percentage of titanium is small, the steel may be dissolved in nitric acid, and the titanium determined colorimetrically after the successive additions of sodium bismuthate, to oxidise any carbonaceous material; and of sulphur dioxide, to reduce any permanganic acid produced by the bismuthate. Phosphoric acid (p. 244) may be used to bleach the colour of the iron. In this case it is important to have in the comparison-tube of the colorimeter a titanium-free steel of otherwise similar composition which has been treated in exactly the same way as the sample. The standard solution of the titanium is added to this solution.

For the Compositions of Typical Steels, see Table I., p. 490.

### **Separations used in Steel Analysis**

As the methods of separation of the elements which may be present in a steel are somewhat confusing, a summary of those in most frequent use is set out below. In certain cases the valencies of the elements are indicated by writing the formulæ of their oxides.

**The Basic Acetate Separation (p. 300).**

$Fe_2O_3$ ,  $Al_2O_3$ ,  $TiO_2$  in the precipitate.

$Cr_2O_3$ ,  $MnO$ ,  $NiO$ ,  $CoO$ ,  $ZnO$ ,  $CaO$ ,  $MgO$ , etc., in the solution.

**The Barium Carbonate Separation.** The cold solution of the metals is made just acid with hydrochloric acid and is then shaken with very

finely-divided barium carbonate. Metals which are easily hydrolysed are precipitated. Sulphates must be absent.

Al,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , Ti, U, V, as hydroxides, are in the precipitate, together with excess of barium carbonate.

MnO, Zn, Co, FeO, Ba, etc., are in the solution.

If the barium carbonate is added to a hot solution, the divalent metals are also partly precipitated.

**The Ether Separation** (p. 312).  $\text{FeCl}_3$  and  $\text{MoCl}_3$  from all other chlorides. These metals are in the ethereal layer.

**The Mercurous Nitrate Separation.** The ore or alloy is fused with sodium carbonate and sodium peroxide, or with potassium nitrate. The aqueous extract is made just acid with nitric acid, or, if potassium nitrate has been used in the fusion, the solution is left slightly alkaline to avoid the production of free nitrous acid, a reducing agent. An aqueous solution of mercurous nitrate, together with an emulsion of mercuric oxide, is then added, the function of the oxide being to remove any slight excess of free nitric acid. After digesting on the hot plate for an hour and filtering, the mercurous salts of  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ , and  $\text{CrO}_3$  will be found in the precipitate, from which the mercury can be removed by ignition.

**Alkali Fusion in Presence of an Oxidising Agent.** As, P, Cr, Mn, Mo, Sb, Si, Sn, Ti, V and W will be found in the aqueous extract.

**Evaporation of a Solution to Dryness with HCl, followed by Extraction with HCl.**  $\text{SiO}_2$  and  $\text{WO}_3$  will be found in the residue.  $\text{MoO}_3$  is practically insoluble in very dilute HCl, but is completely soluble in 20 per cent. HCl.

**Hydrogen Sulphide in Acid Solution.**  $\text{MoS}_3$  is precipitated. This precipitate dissolves in yellow ammonium sulphide. Indeed, hexavalent molybdenum behaves in this respect like tin. Neither tungsten nor vanadium is precipitated from an acid solution of  $\text{H}_2\text{S}$ .

**Cupferron.** This substance is the ammonium salt of nitrosophenylhydroxylamine ( $\text{C}_6\text{H}_5\text{N}\cdot\text{NO}\cdot\text{ONH}_4$ ). In the presence of hydrochloric acid this reagent precipitates ferric iron and titanium, and allows these elements to be separated from Al, Cr, Mn, Ni, Co and Zn.

## PROXIMATE ANALYSIS OF COAL AND COKE

The proximate analysis of coal ordinarily comprises the determination of moisture, ash, sulphur, volatile matter, coke and calorific value.

Since coal usually contains adhering water, which is lost during powdering and preparation for analysis, these determinations are carried out on a sample which has been "air-dried."

A representative portion of the general sample of coal taken for test is finely ground (so as to pass B.S. Sieve No. 72), spread out in a thin layer and allowed to come into equilibrium with the moisture in the air of the laboratory. It is then placed in an air-tight stoppered bottle.

In order to relate the results obtained from the "air-dried sample" to that of the "sample as received," it is necessary to determine the moisture content of the latter. For this purpose, another portion of the general sample is ground so as to pass B.S. Sieve No. 14 and the moisture content of this is determined.

See also p. 254 on "Sampling"; and p. 256 on "Air-drying."

**Moisture.** When coal is heated it gradually loses moisture, but after a time it also undergoes slow oxidation in the air. Since these processes affect the weight of the coal in opposite ways, no determination of moisture in coal which is based on the loss of weight of the sample during heating can be relied upon as being exact. It is generally considered that fairly constant and *relatively* accurate results may be obtained by drying the coal for one hour at a temperature of  $105^{\circ}$  to  $107^{\circ}$  C., care being taken that this temperature is maintained throughout the drying process.

Weigh out 2 grm. of the "air-dried" coal into a shallow, stoppered weighing-bottle. Expose the coal to a uniform temperature of  $105^{\circ}$  to  $107^{\circ}$  C. for one hour; then cool it in a desiccator and weigh it. The above conditions may be attained conveniently in the apparatus described on p. 29, using either toluene or 73 per cent. of glycerin (sp. gr. 1.10) as the liquid in the jacket, which must entirely surround the heating chamber, since the vapour over the liquid will be nearly pure steam at a temperature lower than that required. The use of this mixture avoids any risk which might arise from the inflammability of the toluene vapour.

A more accurate determination of the moisture in coal can be made by heating a sample at  $105^{\circ}$  C. in a current of nitrogen or carbon dioxide in an electrically-heated tube (p. 93), and collecting the water given off in a weighed  $\text{CaCl}_2$  tube.

To determine the moisture in the "sample as received," weigh out 5 grm. in a shallow, stoppered weighing-bottle or Petri dish and heat to constant weight in the oven at  $105^{\circ}$  to  $107^{\circ}$  C. The first weighing should be made at the end of one and a half hours.

**Volatile Matter and Coke.** It is not easy to secure in a laboratory the conditions existing in a retort or coke-oven, and thus to obtain the percentage of coke corresponding with practice. One grm. of air-dried coal is heated in a platinum crucible, 25 to 30 ml. in capacity and covered with a close-fitting lid, for seven minutes over a 20-cm. Bunsen flame. The bottom of the crucible should be 7 cm. above the top of the burner, and the flame should be burning freely and protected from draughts. The under surface of the lid should remain coated with carbon, but the upper surface should be free from it. Cool the crucible rapidly by placing it on a cold iron slab and finally in a desiccator; the loss of weight represents the volatile matter, including moisture.

The weight of the residue in the crucible is the "coke yield." Reserve this residue in the crucible for the determination of the ash. An examination of the coke obtained by this method will indicate whether the original coal is a caking, sintering, or non-caking coal.

*Note.* The Fuel Research Board recommends the use of a platinum crucible of standard dimensions (diameter at base 24 to 25 mm., depth 35 to 40 mm.), supplied with a well-fitting internal capsule lid. The crucible, containing 1 grm. of finely-powdered coal, is placed in a gas or electrically-heated muffle furnace at a temperature of  $925^{\circ} \pm 25^{\circ}$  C.; to minimise the loss due to oxidation, an inert atmosphere is maintained by placing a tray of charcoal inside the muffle and the heating is carried on for seven minutes.

it will melt potassium chromate (M.P.  $940^{\circ}$  C.).

**Ash.** Two methods are usually employed for technical purposes :—

(a) One to 2 grm. of finely-powdered coal in a thin layer are weighed in a shallow platinum, silica or porcelain dish, about 5 cm. in diameter and 1 cm. deep. The dish is heated, gently at first, but finally at a temperature of about  $800^{\circ}\text{C}$ ., in a muffle furnace, in which provision is made for the free circulation of air over the coal. After one hour, the dish is removed, cooled in a desiccator and weighed. To test for completeness of combustion, moisten the ash with a few drops of alcohol. If black specks appear, burn off the alcohol and again ignite.

(b) The coke remaining after the determination of the volatile matter is ignited. For this purpose the crucible lid is removed, the crucible placed well on its side on a triangle and the carbon burnt entirely away over a Bunsen burner. The coke should be stirred occasionally with a platinum wire until the ash is "clean."

**"Fixed Carbon."** This is obtained by deducting the percentage of ash from the percentage of coke.

**Sulphur.** It is often sufficient to determine the total amount of sulphur present in the coal, and the sulphur which is left as sulphate in the ash. The difference between these two figures may be described as "combustible sulphur." For the determination of other forms of sulphur in coal, see the references on p. 519. Two methods are described :

(a) Weigh out accurately about 1 grm. of the finely-powdered, "air-dried" coal and mix it intimately with 3 grm. of Eschka mixture. The latter consists of 2 parts by weight of pure, light, calcined magnesia and 1 part by weight of pure anhydrous sodium carbonate. Both reagents must be free from sulphate. The mixing is carried out in a platinum or porcelain crucible by stirring the powders with a dry glass rod, and the contents of the crucible are then covered with a thin layer of 1 grm. of the Eschka mixture.

Heat the crucible gently at first. Then gradually raise the temperature to dull redness, and continue the heating until the dark colour of the mixture has faded, or has become red owing to the presence of iron oxide ; during the final heating, and not before, the mass should be stirred with a stout platinum or nickel wire. The heating is best carried out in an electric muffle. A spirit lamp may be used, but, if a Bunsen burner has to be employed, the crucible should be fitted into a hole in an asbestos card to prevent the products of combustion of the gas from coming into contact with the contents of the crucible.

When cool, transfer the crucible to a beaker, wash the residue out with about 100 ml. of hot water, add 15 ml. of bromine water and digest on the water-bath for half an hour. Add excess of hydrochloric acid to dissolve the residue, boil to expel the bromine and filter. To 200 ml. of boiling solution add 10 ml. of a 10 per cent. solution of barium chloride and determine the sulphur as  $\text{BaSO}_4$  in the usual way.

A blank determination should be carried out on the Eschka mixture in case it contains sulphates. If a Bunsen burner is used, a blank is essential.

(b) If the bomb calorimeter has been used for determining the calorific value of the coal, the sulphur will have been oxidised to sulphate and the total sulphur can therefore be readily determined in the residue left

case to prevent loss of heat by radiation. The case has openings in its sides through which the progress of the combustion can be watched.

*The following accessories are required for use with the instrument :*

1. An ordinary steel oxygen-cylinder, fitted with a reducing valve.
2. A coil of pipe, preferably of copper, through which the oxygen can be passed before it enters the instrument. This enables the oxygen to be brought to the temperature of the room.
3. A wash-bottle, to indicate the rate at which the oxygen is supplied. The oxygen is passed through this before it enters the calorimeter.

4. A measure of 1000 ml. capacity.

5. A sensitive thermometer, capable of being read, by estimation, to  $0.01^{\circ}\text{C}$ .

6. A 4-volt accumulator with flexible leads to connect it to the ignition terminals; any other suitable source of current may be used.

7. A small silica dish on which the coal or pellet stands during combustion.

8. A compressing-mortar for preparing the coal samples.

**Preparation of Sample.** Thoroughly clean the mould and the plunger of the mortar. Fill the mould with the powdered coal, place it in the press and screw down the plunger as tightly as possible. Then ease the plunger, withdraw the steel plate, and screw the plunger down again until the coal briquette falls through the base of the press. Weigh the sample and place it on the silica dish.

If the-sample is not ground finely enough, it will spark badly in the calorimeter, throwing off pieces of coal, which may then be incompletely burnt.

**General Directions.** Remove the glass chimney of the combustion chamber (Fig. 106) by unscrewing the three milled heads *E* and by turning the top clamping-plate until the slotted lugs are clear of the clamping wires. See that the rubber rings separating the upper and lower clamping-plates from the cylinder are in good condition. Remove the baffle-tube *D* from the base. Put the silica dish with the sample in the centre of the base and replace the baffle-tube in position. Then replace the glass chimney centrally on the rubber ring and screw down the three clamping nuts, applying even pressure. Test the ignition wire by so adjusting the resist-

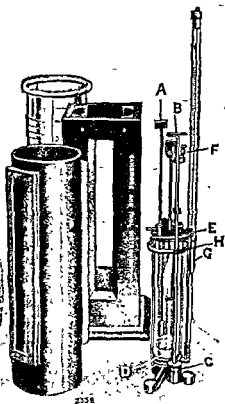


FIG. 106. ROSENBAIN CALORIMETER.

ance that the wire glows sufficiently to ignite the coal when the current has been switched on for one or two seconds. Close the tap *A*, lower the ball-valve *C* by rotating the rod at *B* until the catchpin at *H* drops into the slots, and turn on a small stream of oxygen to prevent any water from entering the chamber through the valve *C*.

Now place the combustion chamber in the calorimeter vessel, which has been previously filled with 2500 ml. of water at a temperature somewhat below that of the room: put the thermometer in the spring fitting attached to the combustion chamber, and increase the oxygen supply until the water is nearly bubbling over the top of the calorimeter; then note the temperature. Now push down the ignition rod with one hand until it touches the sample, and with the other hand switch on the current, slide up the rod, and note the time. The ignition wire will burn through if it is not kept away from the burning sample.

When the sample has finished burning, shut off the oxygen, open the valve *A* and raise the ball-valve *C* to allow the combustion chamber to fill with water. Then close the tap *A* and lower the valve *C*, turn on a stream of oxygen to blow out the water, and allow the water to bubble vigorously for two or three seconds. Now shut off the oxygen, read the thermometer, and continue taking readings at intervals until a maximum reading has been attained; this generally occurs a few seconds after the water has been expelled from the combustion chamber. Note this maximum reading. Also note the total time taken from the time of ignition to the attainment of this maximum temperature. Allow the apparatus to cool with a slow current of oxygen passing for half this time, and note the fall in temperature. Add this fall in temperature, as a radiation correction, to the apparent rise in temperature observed between the initial and maximum readings of the thermometer.

If the water equivalent of the calorimeter has been found (see below), the calorific value can be calculated as follows:

**Example.** *Knowing the water equivalent of the calorimeter, find the calorific value of the coal sample.* If  $x$  be the weight of coal used,  $W$  the water equivalent of the calorimeter,  $w$  the weight of water used, and  $t$  the rise in temperature corrected for radiation, the calorific value  $C$  of the coal used is given by

$$C = \frac{(W + w)t}{x}$$

In a special case:

$x = 1.825$ gm.	Temperature at start	15.41° C.
$W = 345$ gm.	Maximum temperature	20.21° C.
$w = 2400$ gm.	Radiation correction	0.11° C.
$t = 4.77^\circ + 0.11^\circ = 4.88^\circ$		

$$\text{Hence, } C = \frac{(345 + 2400)4.88}{1.825} = \frac{13396}{1.825} = 7340 \text{ calories per gm. of fuel.}$$

The Water Equivalent of the Calorimeter is best determined by burning a known weight of a standard coal in the calorimeter and measuring the rise in temperature. Standard coal briquettes, of known calorific value, can be purchased. Then:

*To find the water equivalent, using a coal sample of known calorific value.*

If  $C$  is known, as when standard samples are used to find the water equivalent, then (from the equation above) :

$$W = \frac{Cx}{t} - w,$$

where	$x = 2.047$ gm.	Temperature at start	$15.30^{\circ} \text{C.}$
	$w = 2400$ gm.	Maximum temperature	$20.82^{\circ} \text{C.}$
	$C = 7500$ calories per gm.	Radiation correction	$0.10^{\circ} \text{C.}$
	$t = 5.52^{\circ} + 0.10^{\circ} \approx 5.62^{\circ} \text{C.}$		

Then  $W = \frac{2.047 \times 7500}{5.62} - 2400 = \frac{15352}{5.62} - 2400 = 2732 - 2400 = 332$  gm.

If the data are given in pounds weight and degrees Fahrenheit the same calculation gives the result in B.Th.U.'s per pound of fuel:

**The Bomb Calorimeter.** The high-pressure oxygen calorimeter, or bomb calorimeter, is the only type of calorimeter which is recognised in standard specifications. It is the most satisfactory type for the following reasons :

The combustion is always complete, provided the proper precautions are observed. The equipment is practically all-metal, so that the transference of heat is very rapid, and none of the products of combustion escape. The loss of heat by radiation is reduced to a minimum and is controlled by the annular water-jacket surrounding the calorimeter. Finally, it can be used for liquid or solid fuel. The bomb of such a calorimeter is shown in Fig. 107. It consists of the following parts :

*A Bomb* or suitable stout-walled combustion chamber, made of metal of great strength, in which the substance is burned (Fig. 107).

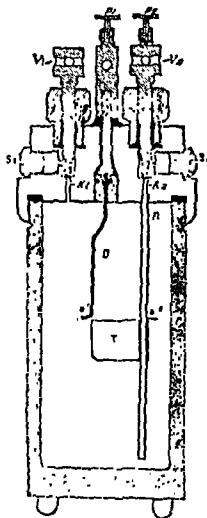
*A Calorimeter* containing water, in which the bomb is immersed and to which the bomb gives up its heat.

*A Centigrade Thermometer* graduated in hundredths of a degree; a lens with cross-wires may be mounted so as to slide up and down the thermometer, permitting readings to  $0.001^{\circ} \text{C.}$  A Beckmann thermometer is suitable.

*A Cylindrical Water-jacket* in which the calorimeter is placed. Attached to this outer jacket is a bracket fitted with friction wheels by means of which a set of mixing paddles may be made to rotate

FIG. 107. THE BERTHELOT-  
MAHLER BOMB CALORIMETER.  
(Krocker's modification).

or move up and down inside the calorimeter. The paddles are operated by hand, or mechanically.



A *Storage Cell, Electric Battery*, or other source of electricity, capable of giving a current of about 2 amps. at 6 volts, for firing the fuel in the bomb.

A *Pressure Gauge*, which records the pressure in the bomb and connecting-tube while the bomb is being charged with oxygen from the steel cylinder. This pressure should not be less than 20 or more than 30 atmospheres.

The interior of the bomb may be protected from the corrosive effects of the acids produced during combustion by a lining of hard enamel. In older forms of the apparatus platinum or gold was employed for the lining, but most modern apparatus is constructed of stainless steel, resistant to corrosion, so that a lining is not necessary. The bomb is fitted with a screw-valve ( $V_2$ ) for regulating the admission of oxygen, and with a support (R) which carries the crucible in which the fuel is placed, and which also serves as one of the terminals ( $P_2$ ) required for the electrical ignition of the substance: a platinum wire (D,  $P_1$ ) is the second terminal. There is also a screw-valve outlet ( $V_1$ ,  $S_1$ ) through which the gaseous products of combustion can be blown out if it is desired to analyse them (see Section XVI). The cover of the bomb can be screwed down securely by suitable means.

The Procedure is as follows: A sample of the finely-powdered coal is made into a pellet by the method described on p. 822 and is then weighed; not more than 1 gm. should be taken.

Ten grammes of distilled water are placed in the bomb, the crucible is fixed into its support, and a piece of platinum wire 0.06 mm. in diameter is looped between the terminals, so that it is in close contact with the coal: a piece of cotton may be threaded round the coal and wire to ensure ignition, a correction being made subsequently for it. The bomb cover is then screwed down and oxygen is admitted very slowly into the bomb until the gauge indicates a pressure of 25 atmospheres. The valve of the oxygen cylinder is then closed, and finally the screw-valve of the bomb is also secured.

The bomb is now placed in the calorimeter containing 2490 gm. of water. This, together with the 10 gm. of water in the bomb, makes a total of 2500 gm. of water. When no oxygen bubbles are seen, showing the joints to be gas-tight, the paddles are kept continuously in motion until the temperature of the water remains constant, as judged by thermometer readings taken at intervals of a minute.

The connecting wires from the battery are then applied to the two terminals. If this has fired the coal, the mercury will shoot up in the stem of the thermometer; the temperature of the water is noted at intervals of a minute until the mercury begins to fall.

The difference between the maximum and the initial temperatures when multiplied by the sum of the weight of the water and the water equivalent of the apparatus, gives the quantity of heat in calories produced by the combustion of the weight of fuel taken. The water equivalent of the apparatus is determined by burning a known weight of some pure combustible substance, the calorific value of which is accurately known; benzoic acid is usually chosen for this purpose.

In testing ordinary fuels the following method of calculation is quite



satisfactory, since careful experiments have shown that it is unnecessary to make any cooling-corrections if the temperature of the water in the calorimeter is the same as that in the water-jacket before the fuel is burnt. If the initial water temperatures are the same as the temperature of the room when the determination is being started, and if

$t^{\circ}\text{C.}$  = the initial temperature immediately before firing,

$T^{\circ}\text{C.}$  = the maximum temperature after firing,

$W$  = the weight of water in the calorimeter,

$w$  = the water equivalent of the apparatus, in grammes,

$w_1$  = the weight in grammes of the fuel taken,

$X$  = the calorific value of the fuel,

$$X = \frac{(W + w) \times (T - t)}{w_1}$$

In more exact work, corrections must be made for heat losses due to cooling and also for gains due to the formation of nitric and sulphuric acids. It is conventionally assumed that when a fuel burns under normal conditions, any nitrogen present is unchanged and sulphur is oxidised to sulphur dioxide. Under the conditions in the bomb, sulphur is oxidised completely with the formation of sulphuric acid; and nitrogen (including atmospheric nitrogen from the air present in the bomb) is converted into nitric acid. Both reactions take place with evolution of a considerable amount of heat. The method of carrying out the determination will, however, in no way be affected. If these corrections are not made, then the error may exceed 50 calories. Refer also to the books listed on p. 519.

Examples of Duplicate Determinations (a, b) are given below :

	a.	b.
Weight of coal (after correction for moisture)	0.8135	0.7938
Initial temperature of water in $^{\circ}\text{C.}$	18.01	18.88
Maximum temperature of water in $^{\circ}\text{C.}$	20.74	20.67
Weight of water in calorimeter in grm.	2500	2500
Water equivalent of apparatus in grm.	712	712

Then the calorific value from (a)

$$= \frac{(2500 + 712) \times (20.74 - 18.01)}{0.8135} = 7228 \text{ calories.}$$

and from (b) the value

$$= \frac{(2500 + 712) \times (20.67 - 18.88)}{0.7938} = 7245 \text{ calories.}$$

Therefore, mean calorific value = 7235 calories.

*Note.* These two results are in good agreement, but it must be remembered that both are uncorrected for cooling losses and that both may therefore be comparatively inaccurate.

## EVALUATION OF FERTILISERS

The value of a manure depends almost entirely on the percentages of phosphorus, nitrogen and potassium it contains, and methods for the determination of these elements are described below. These methods are to some extent based on the *Fertilisers and Feeding Stuffs Regulations* (1932), issued by the Ministry of Agriculture and Fisheries, and these *Regulations* should be consulted for further detailed information.

## Phosphatic Manures

Most of the specimens of natural calcium phosphate, as well as the calcium phosphate present in bones, are insoluble in water, but when these substances are treated with sulphuric acid, the insoluble tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , which they contain is converted into soluble monocalcium phosphate,  $\text{CaH}_2(\text{PO}_4)_2$ . The treatment of insoluble phosphates with sulphuric acid is carried out on a large scale by manure manufacturers to produce the soluble phosphate or "superphosphate" of commerce. "Superphosphate" accordingly consists essentially of monocalcium orthophosphate, but it also contains varying proportions of free phosphoric acid, tricalcium phosphate, dicalcium phosphate, calcium sulphate and compounds of iron, aluminium, magnesium, and the alkali metals, and organic matter is also usually present.

Basic slag or Thomas' phosphate is another common manure. This material is produced in the making of steel by the basic open-hearth or basic Bessemer processes. A layer of lime is spread over the molten pig-iron, and during the process the phosphorus present is oxidised and combines with the lime. Considerable percentages of ferric oxide and silica are also formed. The chemistry of the basic-slag compounds is extremely complicated, but it would appear that there is never very much  $\text{Ca}_3(\text{PO}_4)_2$  present. A considerable proportion of the phosphorus appears to be combined as the complex compound  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaSiO}_3$ . This compound, like much of the phosphorus in basic slag, is soluble in citric acid, while ordinary tricalcium phosphate is not soluble.

Phosphorus in manures is generally classed as :

1. Water-soluble.  $\text{CaH}_2(\text{PO}_4)_2$ ,  $\text{H}_3\text{PO}_4$ .
2. Ammonium citrate-soluble or "reduced."  $\text{CaHPO}_4$ ,  $\text{FePO}_4$ ,  $\text{AlPO}_4$ .
3. Insoluble.  $\text{Ca}_3(\text{PO}_4)_2$ .

As it is considered that the water-soluble phosphate is about thrice as valuable as the insoluble phosphate, and that the citrate-soluble phosphate is inferior to the soluble, but much superior to the insoluble phosphate, the analyst is required to distinguish between the three types.

**Preparation of the Sample for Analysis.** A portion of the sample must be crushed and passed through a sieve with holes 1 mm. square. During this process the water-content of the material will probably change and therefore the moisture in this sample and in the uncrushed portion must be determined. All calculations must be referred to the original coarse manure.

**Moisture.** Weigh out accurately about 8 grm. of the material in a pair of watch-glasses fitted with a clip (Fig. 7, p. 11). Heat at  $100^\circ \text{C}$ . to constant weight ; five hours may be required.

**Water-Soluble Phosphate.** Weigh out accurately about 20 grm. of the fine sample into a litre flask and shake continuously for thirty minutes with 800 ml. of water, in a mechanical shaker. Dilute to 1 litre with water, mix and filter.

Take 50 ml., or a smaller volume, of the filtrate, which should preferably contain 0.1 to 0.3 grm. of  $\text{P}_2\text{O}_5$ , and must not contain more

that basic slag often contains a high percentage of calcium, while in guano the percentage may be low, Table VII., p. 494.) Collect the precipitate and wash it. Weigh the calcium as oxide or titrate it with potassium permanganate (pp. 70 and 158).

When the calcium is determined, proceed as described below.

Sulphate. Heat 100 ml. of solution to boiling and add 10 ml. of 10% solution of sodium carbonate. The sulphate may be determined in a portion of the filtrate from the iron and aluminium.

When the sulphate is determined, proceed as described below.

### Nitrogenous Manures

The nitrogen in nitrogenous manures may be of three kinds, organic, ammoniacal, and "nitric" ( $\text{NO}_3$ ); it is customary to determine these separately, and the method to be employed varies accordingly. Whatever method is used, a blank on 1 grm. of pure cane sugar and the same quantity of reagents must be run in parallel with the determination.

**Total Nitrogen.** The Kjeldahl method (p. 435) is used. The nitric nitrogen is reduced by heating with salicylic acid or phenol, followed by sodium thiosulphate or zinc dust.

Take a suitable weight of the sample in a Kjeldahl flask and add 3 ml. of concentrated sulphuric acid containing 1 grm. of salicylic acid or of phenol. Start shaking the flask immediately and continue for ten minutes; the flask must be kept cool. After ten minutes, add 10 grm. of anhydrous potassium or sodium sulphate and either 5 grm. of sodium thiosulphate crystals or 2 grm. of zinc dust. Add a crystal of copper sulphate to accelerate the reaction and heat until the colour of the solution ceases to fade. After that, continue the heating for one hour. Expel the ammonia, and determine it as is directed on p. 133.

**Ammoniacal Nitrogen.** In the absence of organic nitrogen, weigh out a portion of the manure into a standard flask. Shake up with water and dilute to the mark. Determine the ammonia in a suitable volume of this solution by the method given on p. 133.

In the presence of organic nitrogen, weigh out a portion of sample into a distillation-flask. Add 200 ml. of water and 5 grm. of magnesium oxide, which must be free from carbonates. Distil the ammonia into standard acid and determine it in the usual way. Organic nitrogen is not decomposed by magnesia, but sodium or potassium hydroxide will wholly or partly decompose it.

**Nitrate and Ammoniacal Nitrogen.** In the absence of organic matter, the nitrate with Devarda's alloy and determine the total ammonia (pp. 84 and 133).

Alternatively, dissolve 10 grm. of the fertiliser in water and dilute to 500 ml. Take 50 ml. of this solution in a 500-ml. conical flask, which is closed by a rubber stopper which carries a thistle funnel half-filled with glass beads. Add 10 grm. of "reduced iron" (sold as *Ferrum Reductum*) and 20 ml. of sulphuric acid (sp. gr. 1.35). When all effervescence has ceased, boil for five minutes, wash down the beads, and boil the solution for a further three minutes. Distil with sodium hydroxide.

In the presence of organic nitrogen, use the method described immediately above, but distil with magnesium oxide.

**Organic and Ammoniacal Nitrogen.** In the absence of nitric nitrogen, add 25 ml. of concentrated sulphuric acid to the weighed sample in a Kjeldahl flask. Heat gently until frothing ceases. Add 10 grm. of anhydrous sodium or potassium sulphate and a crystal of copper sulphate. Heat until the colour remains unchanged, and after that for one hour. Distil with sodium hydroxide.

### Potash Manures

**Potassium. Preparation of Solution.** The methods laid down by the Ministry of Agriculture and Fisheries are as follows :

In the absence of sulphate, phosphate, iron, etc., take a weighed portion of the sample containing 1.5 to 2 grm. of  $K_2O$ . Dissolve it in water, filter if necessary, and make up the solution to 500 ml. Determine the potassium in 50 ml. of this standard solution by the perchlorate method (see below).

In the presence of sulphate, but in the absence of phosphate, iron, etc., the standard solution for analysis is to be prepared as follows : As before, take a portion containing 1.5 to 2 grm. of  $K_2O$ . Boil it with 300 ml. of water and 20 ml. of concentrated hydrochloric acid, and to the boiling solution add a solution of barium chloride dropwise until all the sulphate radical has been precipitated. Cool, and dilute to 500 ml. Filter, and take 50 ml. of the filtrate. Evaporate this portion to dryness. Cool. Add concentrated hydrochloric acid and again evaporate to dryness. Dissolve the residue in a little dilute hydrochloric acid, filtering if necessary, and determine the potassium in it by the perchlorate method.

For the determination of the potassium in guanos, or in other manures containing phosphate, iron, etc., take 10 grm. of the sample and ignite gently to remove organic matter. Heat the residue for ten minutes with 10 ml. of concentrated hydrochloric acid and then add 300 ml. of water and boil. Filter, and add powdered, solid barium hydroxide to the boiling filtrate until the liquid is slightly alkaline. Cool, and make up to 500 ml. Filter again. Take half this filtrate and add ammonia and ammonium carbonate to it in excess. Raise the liquid to its boiling-point, and add powdered, solid ammonium oxalate in excess. Cool. Make up to 500 ml. and filter.

Take 100 ml. of this solution in a porcelain dish, and evaporate the liquid to dryness. Heat the solid residue in the dish gently (never above low redness) until all the ammonium salts have disappeared. Cool. Moisten the residue with concentrated hydrochloric acid and again evaporate to dryness. Extract the soluble portion with dilute hydrochloric acid, and filter.

**Precipitation of the Potassium as Perchlorate.** The solution, prepared by one of the processes described above, is placed in a small basin. To it add 7 ml. of 20 per cent. perchloric acid (sp. gr. 1.125), and heat the liquid on a hotplate or sand-bath until white fumes are evolved copiously. Cool somewhat, and dissolve the precipitate in hot water. Add a few drops of the perchloric acid and concentrate the solution again. Cool, and proceed as described on p. 82.

*Note.* For the determination of potassium in guano and other complex manures, the modified chloroplatinate method, though unofficial, is to be pre-

salts are extracted with dilute hydrochloric acid and the solution, after filtering, is ready for treatment with chloroplatinic acid. The precipitated potassium

### Other Fertilisers

**Free Acid in Ammonium Sulphate.** Dissolve 20 gm. of the salt in 50 ml. of water. Filter. Dilute the solution to about 250 ml. with water and titrate with decinormal sodium hydroxide using 2 or 3 drops of an aqueous 0.05 per cent. solution of methyl orange as indicator.

**Lime in Burnt Lime and in Hydrated Lime.** Grind the sample rapidly and pass it through a sieve in which the holes are approximately 0.2 mm. square. Transfer 5 gm. to a stoppered bottle of 1 litre capacity. Add 10 ml. of alcohol and 400 ml. of a 10 per cent. solution of cane sugar, and shake the bottle mechanically for four hours. The alcohol and the sugar solution must first be tested to ensure that they are neutral to phenolphthalein, and their acidity must be adjusted if necessary.

Filter the solution through dry paper into a dry vessel, and titrate 50 ml. of the filtrate with seminormal hydrochloric acid, using phenolphthalein as indicator.

**Calcium Carbonate in Ground Chalk, Limestone and Carbonate.** Add dilute hydrochloric acid to a weighed quantity of the sample until there is no further effervescence. Filter the solution and wash the residue. If iron, aluminium and other interfering elements are present in the solution, they must be removed (pp. 270 and 271). Precipitate the calcium in the filtrate as calcium oxalate and weigh it as calcium oxide (p. 70).

Determine the weight of carbon dioxide evolved when a weighed quantity of the sample is treated with dilute hydrochloric acid (p. 70).

The percentage of calcium carbonate in the material is calculated both from the calcium and from the carbon dioxide content; the smaller percentage is returned.

### EVALUATION OF TANNING MATERIALS

The determination of tannin in natural tanning materials is complicated by the facts that there is often present in the same substance a mixture

of different tannins ; and that other compounds which affect the accuracy of the determination are always present. No method gives results of scientific accuracy, but two methods which are employed for technical purposes are described below.

In the first of these, a gravimetric method, the tannin in the water-extract of a known weight of the tanning material combines with hide-powder which has undergone a preliminary treatment of "chroming." It is necessary for this purpose to evaporate a portion of the extract or infusion of the tanning material and to determine the total amount of matter in solution : then to remove by hide-powder the tannin from another portion of the extract and again to determine the matter in solution : the loss of weight is due to the removal of the tannin by the hide-powder and hence the amount of the tannin can be estimated.

The following results were obtained from four samples of oak-wood extract :

Percentage of	A	B	C	D
Total soluble matter . . .	41.3	35.0	37.8	38.1
Soluble non-tanning matter . .	14.1	4.7	14.0	4.8
Soluble tanning matter . . .	27.2	30.3	23.8	33.3

This method is the more suitable for the tanner, since it estimates directly the amount of tannin which is involved in tanning a skin. It is generally adopted for the evaluation of tanning materials, and is the officially-recognised method of the International Society of Leather Trades' Chemists.

The other method, proposed by Löwenthal, estimates the tannin by its reducing effect under suitable conditions upon standard potassium permanganate solution. It is of limited value and is now mainly employed for the control of tannery liquors.

**General Directions for the Preparation of the Extract or Solution.** The tanning material is either supplied in its natural state ; or the soluble matter is supplied either as a liquid extract, or as "solid extract," which is the solid residue remaining after the water-extract has been evaporated.

The infusion of the tanning material, which is to be used for the hide-powder process, must contain as nearly as possible 4 grm. of tanning matter per litre, and not less than 3.5 nor more than 4.5 grm. The weights of different tanning materials to be extracted by a litre of water, or to be diluted to a litre, in order to obtain an infusion of suitable concentration, are tabulated below :

BARKS, ETC.		EXTRACTS.	
	Grm.		Grm.
Algarobilla . . . .	8-9	Oakwood, sp. gr. 1.2 or over .	16-18
Canaigre . . . .	15-18	Chestnut (liquid) . . . .	14
Divi-divi . . . .	9	Chestnut (solid) . . . .	7
Hemlock-bark . . . .	32-36	Quebracho (solid) . . . .	6
Mimosa-bark . . . .	11	Quebracho (liquid) . . . .	0-13
Myrobalans . . . .	15	Mimosa D . . . .	10-12
Oak-bark . . . .	30-36	Gambier (block) . . . .	12-14

## BARKS, ETC.

	Grm.
Oak-wood . . . . .	50-100
Quebracho-wood . . . . .	20-22
Sumach . . . . .	15-16
Pistacia-lentiscus . . . . .	20-22
Pine-bark . . . . .	32
Willow-bark . . . . .	36
Chestnut-wood . . . . .	45
Mangrove-bark . . . . .	10
Valonia . . . . .	14-15
Valonia-beard . . . . .	10-11
Spent tans . . . . .	50-100

## EXTRACTS.

	Grm.
Gambier (cube) . . . . .	7
Mangrove (liquid) . . . . .	9
Mangrove (solid) . . . . .	7
Cutch . . . . .	7
Myrobalans (liquid) . . . . .	16
Hemlock . . . . .	10-14
Pine-bark . . . . .	16

A Natural Solid Tanning Material must first be well sampled and then suitably broken up and ground until it will pass through a wire sieve of 5 strands per centimetre. The soluble matter is then removed from a suitable quantity (see Table above) in a Procter extractor (see below) by treatment with 500 ml. of water at a temperature not exceeding 50° C., and the extraction is continued with boiling water until the filtrate amounts to 1 litre. The best temperature for extraction differs materially with different samples. When this temperature is not known, it is generally best to begin at about 35° C., and then to raise the temperature to 100° C. as the operation proceeds. It is desirable to allow the material to soak for some hours before the percolation commences, and, in order to extract the maximum amount of tannin, the percolation should take not less than three hours. Any soluble matter remaining in the material is neglected, or is reported separately as "difficultly soluble" matter. The volume of cold liquid in the flask is made up accurately to 1 litre.

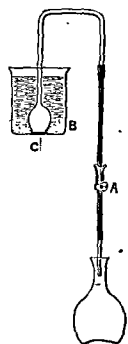


FIG. 108. PROCTER EXTRACTOR.

A Liquid Extract is weighed in a basin or beaker and is washed with boiling distilled water into a litre flask; the flask is then filled up to the mark with boiling water, well mixed, and rapidly cooled to a temperature of 17.5° C., and the contents are accurately made up to the mark, again well mixed, and filtered if necessary as is directed below. Sumach and myrobalans extracts should be dissolved at lower temperature.

A Solid Extract is dissolved by beaker with of The soluble port into the undissolved it has treated with the whole of treatment of liquid extract.

The Procter solid tanning Fig. 108. The

vessel. An ordinary thistle funnel serves as a siphon to draw

funnel has muslin tied over it and is placed on the bottom of the beaker, and the funnel is held in position by a clamp. A layer of dry sand, which has been purified by treatment with hydrochloric acid followed by thorough washing with water, is poured upon the bottom of the beaker to a depth of 2 cm. so as to cover the mouth of the funnel. The prepared and dried tanning material is mixed with the water in which it is to be digested and the liquid poured over the sand.

After the digestion with water has continued at the ordinary temperature for some hours, conveniently overnight, the extract is siphoned over. This is accomplished by attaching a narrow glass tube about 15 cm. long to the arm of the funnel by means of a short piece of narrow rubber tube provided with a pinch clamp (A). The tube is filled by suction, and the clear extract, as it siphons over, is collected in a flask. The extraction of the tanning material is finished by pouring successive quantities of fresh water into the beaker and siphoning them over. When 500 ml. have been collected, the beaker is immersed in a boiling water-bath. The process is complete when 1,000 ml. have been collected in three hours, the liquid passing over at the rate of about 5 ml. per minute.

**Filtration.** Solutions of tanning materials frequently become turbid on cooling even if they were clear while hot, and they must be filtered carefully, usually by passing them through a special Berkefeld candle-filter connected to a vacuum-pump. After the vacuum has been formed in the flask, the connection between it and the pump must be closed in order to minimise loss of liquid by evaporation. At least 200 to 300 ml. of the first part of the filtrate, more if necessary, should be rejected in order to obtain an absolutely clear and brilliant filtrate. The infusion must be optically clear; it must not be merely transparent, but must show no opalescence when the vessel is placed on black paper in a good light. If necessary, the solution must be filtered several times.

**"Total Soluble" Matter.** Fifty millilitres of the filtered infusion are measured into a weighed flat-bottomed porcelain, glass or platinum dish, of diameter of not less than 6.5 cm. The liquid is evaporated to dryness on a water-bath and the residue is heated in a vacuum-oven at 100° C. or in a steam-oven until it is constant in weight. The dish is subsequently cooled in a desiccator over calcium chloride for twenty minutes and weighed. Weighing should be carried out rapidly to avoid absorption of moisture.

The weight of the residue multiplied by 20 gives the "total soluble" matter derived from the tanning material taken for extraction, and hence the percentage can be calculated.

**Note.** To determine the "total solids," of a uniformly turbid solution, it is convenient to draw off 50 ml. of the well-mixed and unfiltered solution with a pipette. The residue of material taken gives the "moisture content."

**Correction for Absorption of Tannin-Matter by the Filter** is not needed for the Berkefeld candle, or for a Whatman No. 11 filter-paper, if from 250 to 300 ml. of the filtrate are rejected.

**Preparation of the Hide-powder by "Chroming."** The hide-powder should be of woolly texture and should conform to the following test:



Not more than 5 ml. or less than 2.5 ml. of a 0.1 N. solution of NaOH or KOH should be required to produce a permanent pink colour with phenolphthalein when added to 6.5 gm. of the dry powder, suspended in water. If the acidity does not fall within these limits, it must be adjusted, before "chroming," by soaking the powder for twenty minutes in from ten to twelve times its weight of water, to which the calculated quantity of standard alkali or acid has been added.

The hide-powder must not swell during the "chroming" process to such an extent as to render difficult the pressing operation described below, and it must be nearly free from soluble organic matter. During the determination of a tannin, the weight of soluble organic matter, which can be extracted from the chromed powder by each 100 ml. of tannin solution, should not exceed 5 milligrams. This may be determined by carrying out a blank experiment, using distilled water in place of the tannin extract (*Note 1*).

The hide-powder should be air-dried before it is used, and its moisture content is first determined; this will remain practically constant if the powder is kept in an air-tight vessel. That weight of hide-powder which corresponds with 6.5 gm. of the dry powder is then taken and wetted with approximately ten times its weight of distilled water.

Meanwhile a solution of basic chromium chloride is made by dissolving 2 gm. of crystallised chromic chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) in water and adding 11.25 ml. of normal sodium carbonate solution: this changes half the chromic chloride into chromium hydroxide,  $\text{Cr}(\text{OH})_3$ , which remains in solution in the excess of  $\text{CrCl}_3$ . The total volume of solution so made will "chrome" 100 gm. of dry hide-powder. The calculated volume of the basic chromic chloride solution for 6.5 gm. of dry powder is added to the suspension of hide-powder in water, and the whole is mixed by churning slowly for an hour.

At the end of an hour the wet hide-powder is squeezed in linen to free it so far as possible from the residual liquor, and it is then washed repeatedly with distilled water and squeezed until the addition of a drop of 10 per cent.  $\text{K}_2\text{CrO}_4$  solution and 2 drops of decinormal  $\text{AgNO}_3$  solution to 50 ml. of the last filtrate produces a brick-red coloration. Four or five squeezings are usually sufficient, but more may be necessary. Such a filtrate cannot contain more than 0.001 gm. of NaCl in 100 ml. The powder is then squeezed in a press until it contains from 70 to 75 per cent. of water, and it is then weighed.

**Procedure.** The detanninisation of part of the tannin extract is effected by weighing out that quantity (*Q*) of the chromed powder which contains 6.5 gm. of the dry powder; this is added immediately (*Note 3*) to 100 ml. of the unfiltered tannin infusion, together with  $(26.5 - Q)$  gm. of distilled water and 1 gm. of kaolin freed from soluble matter. The addition of this volume of water dilutes the original 100 ml. of infusion to 120 ml. The whole is agitated for fifteen minutes in a corked bottle. If a rotating frame is used, the bottle should rotate not less than sixty times per minute, but any satisfactory method of vigorous shaking can be adopted. The contents are then squeezed immediately through linen, stirred and filtered through a folded filter-paper of sufficient size to hold the entire filtrate; the filtrate is returned to the filter repeatedly until

it is clear, and 60 ml. are then evaporated to dryness by the method described on p. 335, the weight of the dried residue being determined.

This gives the weight of residue obtained from 50 ml. of the original infusion after removal of the tannins, i.e., the weight of "non-tannins." The difference between this weight and the weight of "total soluble" matter obtained on evaporation of 50 ml. of the filtered infusion (p. 335) gives the weight of "tannins" in 50 ml. of infusion. From this the percentage weight of tannins in the sample of tanning material can be calculated.

*Note 1.* Hide-powder, which has been tested by a special committee of the International Society of Leather Trades' Chemists, is obtainable.

*Note 2.* In laboratories where analyses are continually being made, it is more convenient to keep a 10 per cent. stock solution of the chroming liquid. This  
 . . . . . litre  
 . . . . . very  
 . . . . . with  
 . . . . . ld be  
 used for 100 grm., or 1.3 ml. for 0.5 grm. of the dry powder.

*Note 3.* The moist hide-powder should not be kept for more than a few hours before it is used. If the non-tannin filtrate gives a turbidity when it is mixed with a drop of a solution containing 1 per cent. of gelatin and 10 per cent. of salt, further hide-powder is necessary.

The Analysis of Used Liquors and of Spent Tans should be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being either diluted, or concentrated by boiling *in vacuo* or in a vessel to which access of air is restricted, until the amount of "tanning matter" is preferably between 3.5 and 4.5 grm. per litre; however, in no case must the amount of "total solids" present exceed 10 grm. per litre.

**The Löwenthal or Permanganate Method.** This method can only be used for comparing the relative tanning-values of different specimens of the same tanning material; it is useless for comparing the relative tanning-values of different kinds of tanning materials.

Potassium permanganate solution is readily reduced by a solution of tannin, and the relative reducing powers of the different varieties of tannin have been determined. Accordingly if the tannin, free from other oxidisable matter, could be extracted from the tanning material, the amount present could be readily determined by titrating the extract with standard permanganate solution. An extract of a tanning material, however, invariably contains other substances, besides tannin, which reduce permanganate. Hence it is necessary first to titrate a portion of the extract with permanganate, and then to titrate a second portion of the extract from which the tannin has been removed. The difference between the volumes of permanganate solution which are required in the two titrations represents the volume of the permanganate solution which has been required for the oxidation of the tannin.

In order to limit and make definite the oxidising action of the permanganate on the oxidisable matter, a known volume of indigo-carmin solution is added to the extract, followed by the permanganate solution, until the blue colour of the liquid changes to a clear yellow.

The following solutions are required for the Löwenthal method:

(a) *Standard Potassium Permanganate Solution.* Half a gramme of pure permanganate is dissolved in water and the solution is diluted to

1 litre; if many titrations have to be made, it is better to dilute 100 ml. of a solution containing 5 grm. per litre, as required.

(b) *Solution of Pure Indigo-Carmine.* This is prepared by dissolving 5 grm. of pure, dry sodium or potassium sulphindigotate (Carminum cærul. opt.) in distilled water; 50 grm. of pure sulphuric acid are added, the solution is diluted to 1 litre, and is filtered if necessary.

(c) *A Solution of Gelatin* is made by allowing 2 grm. of thin sheets of the purest gelatin to soak in cold distilled water for a few minutes. The washing water is rejected and the gelatin finally dissolved by heating it upon a water-bath with enough water to make up the solution to about 100 ml. This solution should be made shortly before it is required for use, since it may deteriorate on keeping.

(d) *Kaolin*, purified by powdering and washing.

(e) *Sodium Chloride Solution.* A saturated solution containing 50 ml. of concentrated sulphuric acid per litre.

**Procedure.** A sample of sumach is evaluated as follows: First, the actual tannin-value of the permanganate solution is determined by titrating it with a solution of gallic acid under exactly the same conditions as those under which the tanning material is subsequently to be titrated. For this purpose, a solution of 0.1 grm. of pure, crystallised gallic acid in 100 ml. of water is used as a standard, and the amount of tannin to which 1 grm. of gallic acid is equivalent is obtained from the Table on p. 340. In this particular case, 1 grm. of gallic acid is equivalent to 1.50 grm. of sumach-tannin.

About 750 ml. of distilled water are placed in a large beaker on a white tile, 25 ml. of the indigo solution (b) are added, and the whole is titrated with the permanganate solution (a). About 25 to 30 ml. of the permanganate should be required. The mean of two titrations is taken and gives the "indigo value." The titration is repeated using 25 ml. of the indigo solution and 5 ml. of the standard gallic acid solution. The mean of two titrations is again taken, and, if the "indigo value" is subtracted from the result, the "gallic acid value" of the permanganate is obtained.

An extract of from 15 to 16 grm. of sumach is prepared according to the directions given (p. 334), and 5 ml. of the filtrate, or less if necessary, are measured into a litre beaker, together with 25 ml. of the indigo solution (b), and 750 ml. of distilled water. The permanganate solution (a) is added from a burette until the blue colour of the solution begins to change to green. The addition must be made at a constant rate, and the liquids must be mixed well by vigorous stirring during the whole titration.

As soon as a green tint appears, the permanganate is added much more slowly until the solution assumes a dirty greenish-yellow colour. It is best at this stage to allow the liquid to stand for a moment or two, and then to add the permanganate, 1 or 2 drops at a time, and to stir vigorously after each addition. This procedure is continued until the liquid in the beaker assumes a clear yellow colour. This titration should then be repeated, and the two results thus obtained should not differ by more than 0.1 ml. The end-point is made more certain if the liquid from the first titration is kept, and care is taken that the tint finally obtained in subsequent titrations matches it exactly; this ensures that all titrations

are carried to the same stage. A constant error may be introduced, but this will not affect the final result. The titration can be made by artificial light diffused by passage through ground glass or tissue paper, but, as the end-point is slightly different with different forms of lighting, the whole of an analysis must be made under the same conditions of illumination. This titration corresponds with the total amount of oxidisable matter, both tannin and non-tannin, which is present in the sumach.

It is now necessary to remove the tannin from a portion of the solution, in order to determine the non-tannin matter separately. For many purposes hide-powder, as is described under *Detannisation* on p. 336, may be used to remove the tannin; but this may also be effected by means of gelatin, as is described below (see *Note*).

Fifty millilitres of the original, filtered solution of the sumach are introduced into a 100-ml. stoppered measuring-cylinder, 25 ml. of the gelatin solution (c) and 25 ml. of the acidified salt solution (e) are added, and the liquids are shaken well. A teaspoonful of kaolin (d) is then added to facilitate the filtration, and the liquid is filtered.

Ten millilitres of the filtrate, corresponding with 5 ml. of the original solution, are titrated with the permanganate as is described above. Since the gelatin, in the presence of salt and sulphuric acid, precipitates the tannin-matter, it is evident that the difference between the result of this titration and of that already carried out on the untreated extract will give the amount of permanganate solution which has been reduced by the tannin-matter itself. From this result the percentage of tannin may be calculated as described below.

#### The Following Precautions must be observed in the Löwenthal Method.

1. If the gelatin, kaolin, or salt, used to precipitate the tannin, contains

are used in a titration. The mixture is made up to 100 ml., filtered, and 20 ml. of the filtrate are titrated with the permanganate. If the volume of permanganate used exceeds by more than 0.1 ml. that required by the indigo solution alone, then one-half of this excess must be deducted from the result obtained by the titration of the oxidisable non-tannin matter, before this is subtracted from the result representing the total oxidisable matter present in the extract.

2. The indigo solution in this method serves not only as an indicator, but it also controls the oxidising action of the permanganate by keeping it within certain definite limits. In order to ensure a uniform limiting action, the volume of the permanganate solution which is used in a titration must never much exceed one and two-third times that which is required by the indigo alone; if this quantity is exceeded, the tannin solution must either be diluted or a smaller volume of it must be taken and the titration must be repeated.

3. If the titrations are not carried out in a strictly parallel manner as regards stirring and rate of addition of the permanganate, comparable results cannot be obtained, since the procedure during titration considerably affects the ultimate result.

**Calculation for Löwenthal Analysis of Sumach.** Fifteen grammes of sumach per litre were used. Twenty-five ml. of the indigo solution with 2.5 ml. of the sumach infusion required in two titrations 41.35 and 41.25 ml. of permanganate, or an average of 41.3 ml. Twenty-five ml. of the indigo solution alone required 14.6 ml., After detannising with 25 ml. of the

indigo solution and required 28.7 ml. of permanganate. Accordingly 5 ml. of the original sumach solution after detannising required  $28.7 - 26.7 = 2$  ml. of permanganate, and hence 10 ml. of the original solution would require 4 ml. The volume of the permanganate solution required for the tannin in 10 ml. is therefore  $58.4 - 40 = 18.4$  ml.

Similarly two 5-ml. portions of the gallic acid solution, which are together equal to 10 ml. of the 1 grm. per litre solution, required 19.4 ml. of the permanganate. Now 1 grm. of gallic acid is shown by the Table below to be equivalent to 1.5 grm. of sumach-tannin, and the gallic acid solution is therefore equivalent to a solution containing 1.5 grm. per litre of sumach-tannin. Accordingly.

$$18.4 : 54.4 \times \frac{100}{15} :: 1.5 : 28 \text{ per cent.}$$

i.e., the sumach contained 28 per cent. of tannin.

*Note.* In the Löwenthal method, shaking with chromed hide-powder is generally to be preferred to precipitation with gelatin, since the results of the former method agree more closely with those obtained by the gravimetric method (p. 336). The factor to be used in the calculation may be obtained from the Table below, but this is more safely found by direct determination.

**Determination of the Absolute Percentage of any Form of Tannin.** If it is desired to determine the actual percentage by weight of any form of tannin, other than gallotannic acid, in a sample of tanning material by the Löwenthal method, it is necessary to standardise the permanganate solution by the gravimetric method already described (p. 336).

Five ml. of the original extract are titrated as directed above; 6 ml., representing 5 ml. of the same extract after detannisation, are also titrated to obtain the amount of non-tannin matter present. Fifty ml. of the original extract and 60 ml. of the filtrate from the hide-powder are then evaporated separately, and the residues are dried as directed and weighed. The actual weight of the tannin matter, which corresponds with the gallic acid equivalent of the permanganate used, can then be calculated and a factor obtained.

This method is obviously convenient only when a number of titrations of similar tannin solutions are being made. In some cases the proportion of oxidisable non-tanning matter can be assumed to be constant, and the tannin-strength of a liquor is then obtained by a single titration.

Table of Average Factors for Löwenthal's Method

Material	Weight of tannin in grammes, equivalent to 1 grm. of gallic acid.
Chestnut-wood tannin	1.65
Oak-wood tannin	1.89
Myrobalans tannin	1.73
Quebracho-wood tannin	1.60
Valonia	1.58
Sumach	1.50
Oak-bark	1.71
Mimosa-bark	1.88
Mangrove-bark	1.46
Gambier cube	1.78
Average of all above materials	1.69

## DRY ASSAY OF ORES OF LEAD, SILVER, GOLD AND TIN

The dry assay of Lead Oxides and Ores is carried out very quickly, but even under good conditions it gives only approximate results. If the ore contains only a small percentage of lead the method is useless. On the other hand,

with rich ores, the dry assay probably gives a better indication of the lead which can be extracted from the ore on a technical scale than does the more exact wet assay. Most lead ores contain traces of silver, which can be determined more exactly by the dry assay than by any other method.

**Dry Assay of Galena for Lead.** The ore is reduced by heating it with iron and with a suitable flux, and the metallic lead thus separated is weighed. Either iron may be introduced into a clay crucible (a), or an iron crucible may be employed (b).



(a) *Assay of Galena in a Clay Crucible.* Grind the sample of ore in a mortar until the whole of it passes through at least a B.S. 72-sieve.

Weigh out 25 grm. of the ore, 25 grm. of anhydrous sodium carbonate, 3 grm. of potassium hydrogen tartrate, and 4 grm. of borax, the latter being added to increase the fluidity of the flux and to protect the crucible from attack by the molten sodium carbonate.

Reserve one-fifth of the sodium carbonate; mix the remainder with the ore and with the tartrate on a large sheet of paper or of American cloth by causing the various solids to run into each other by suitably manipulating the sheet. Continue the mixing until the mass is uniform in colour, and then transfer it to the crucible. Wash off the paper with the reserved sodium carbonate, adding the residues to the crucible. Then add a layer of the borax as a seal. Double over a piece of clean hoop-iron, of such a length that when bent it will just fit into the closed crucible, into the form of a U, and place it in the mixture with the free ends downwards. Place the crucible low down in a dull-red fire, and cover it with a lid.

Raise the temperature gradually and after twenty minutes, or when bubbles of gas are no longer coming away freely from the melt, grasp the hoop-iron with the tongs in such a way that the ends of the iron are not forced together, so trapping some lead, and stir the mixture with it. Tap the tongs sharply against the side of the furnace to remove any lead which may be sticking to the iron, and withdraw the iron.

Cover the crucible again and heat it more strongly for five minutes to render the slag more fluid. Remove the crucible from the furnace, swing it round two or three times to collect the lead into a globule, tap it on the floor, and pour the melt into a conical iron mould which has been very lightly dressed with oil. Wait until the lead has entirely solidified, a process which takes a surprisingly long time, and then turn the button out of the mould. Detach the slag by hammering it lightly on an anvil. The button should be hit on the edge, not on the flat, or the slag will be hammered into the metal. Most of the slag will be removed if the button is hammered into the shape of a hexagon. Then clean the button by warming it for some time in dilute sulphuric acid and, after the small pieces of slag have been loosened by the acid, by scrubbing it with a hard brush. Dry, weigh, and retain it for the determination of silver by cupellation.

(b) *Assay in an Iron Crucible.* Weigh out 25 grm. of the finely-powdered ore, and mix them with 25 grm. of anhydrous sodium carbonate and 3 grm.

of crude tartar. Heat a scraped wrought-iron crucible to dull redness in a wind-furnace, remove the crucible, introduce the above mixture, and cover its surface with a sprinkling of borax. Cover the crucible with a lid, replace it in the furnace, and surround and cover it with coke.

Heat the crucible moderately for about twenty minutes, taking care not to let the temperature rise too high; then remove it from the furnace, and scrape down any slag adhering to the sides with an iron stirrer. Swing the crucible, tap it gently, and pour the molten mass into a smooth, conical, iron mould. Prepare the lead button for weighing as in (a) above.

After the fused mass has been poured out, the internal surface of the crucible should be smooth and no globules of lead or of partly fused portions of slag should be seen adhering to the interior. The slag should be homogeneous, and should contain no particles of lead or of undecomposed galena. The mean of several assays should be taken. A wrought-iron crucible will serve for from ten to twenty assays.

**Assay of Oxides of Lead.** The dry assay of  $\text{PbO}$  or  $\text{Pb}_3\text{O}_4$  may be made with the following reducing mixtures:

For $\text{PbO}$ .				For $\text{Pb}_3\text{O}_4$ .			
$\text{PbO}$	.	.	40 grm.	$\text{Pb}_3\text{O}_4$	.	.	40 grm.
$\text{Na}_2\text{CO}_3$	.	.	30 "	$\text{Na}_2\text{CO}_3$	.	.	30 "
Borax	.	.	10 "	Borax	.	.	10 "
Flour	.	.	8 "	Flour	.	.	10 "

The flour is a convenient source of finely-divided carbon.

The mixture is fused in a clay crucible in a wind-furnace, avoiding too high a temperature which might cause loss of lead by volatilisation.

The temperature is raised slowly and maintained at a dull-red heat for twenty minutes. The crucible is then heated to a somewhat higher temperature for five minutes to render the slag more fluid. The crucible is withdrawn, swung, tapped and poured, and the button of lead is cleaned in the same way as described under (a).

The weight of silver present in the lead oxide may be found by cupelling this button. This must be known when the oxide is used in the assaying of silver and gold.

**Assay of Carbonate of Lead.** Weigh out 30 material. Mix them with 20 grm. of sodium of tartar (potassium hydrogen tartrate), powdered charcoal; place the mixture in a and proceed as is described on 341.

finely-powdered  
grm. of cream  
of finely-  
clay

The lead containing bone ash, bauxite, or cupel, and is heated products of current of air can be converted into oxide, the cupel. The silver which is

for

known  
from  
The

**Scorification.** When the silver content of the lead is small, or if for any other reason the quantity of lead to be assayed is large, the weight of that metal must be reduced before cupellation. The process of scorification is used. A scorifier is a small, shallow dish of fireclay.

The scorifier is heated to bright redness in a muffle, from which the spent gases are excluded and which is so arranged that a steady stream of air is pulled over the dish. When the dish is hot, the lead is dropped into it. The lead melts at once and oxidises to  $\text{PbO}$ , which is liquid at the temperature used. This litharge attacks the silica of the scorifier to some extent and the lead silicate renders the slag more fluid.

When only about 20 grm. of metallic lead remain, the slag may be cleaned by placing on its surface 0.2 grm. of powdered charcoal wrapped in tissue paper. A small quantity of lead silicate is thus reduced and the globules of lead formed collect any silver present in the slag and carry it to the main mass of metal. Such silver is usually so minute in quantity that this step can be safely omitted. The contents of the scorifier are then poured into a button-mould. When the lead, which should weigh about 20 grm., is quite solid, the button is cleaned by gentle hammering. It contains all the silver originally present in the sample of lead and is ready for cupellation.

**The Process of Cupellation.** The weight of the cupels used, if they are of bone ash, should be at least  $1\frac{1}{4}$  times the weight of the lead button. Cupels of other material are generally less absorbent than those of bone ash.

Place the cupels in the muffle and maintain them at a bright red heat for at least a quarter of an hour to drive off moisture and to prepare them for the lead. They should be so nearly at the temperature of the muffle that they are difficult to see. Drop the button of lead into the heated cupel by means of the assay tongs, and close the muffle door. A black crust will form on the surface of the lead, but this will disappear in a short time, leaving the button brighter than the cupel. If this "clearing" does not take place, drop a little powdered charcoal, wrapped in tissue-paper, into the cupel and raise the temperature of the muffle. If the "clearing" does not now appear, start with a fresh button, and use a higher temperature.

As soon as the button is "clear," reduce the draught of the furnace, and allow a little air to enter by the muffle door; also let the temperature fall somewhat, since the temperature at starting is higher than is needed during the oxidation of the lead, and might volatilise some of the silver. Towards the end of the process, raise the temperature again by closing the muffle door and increasing the draught.

The final stage is easily recognised, since the thin layer of oxide is reduced to a film producing iridescent colours, and these suddenly disappear when the operation is finished. The sudden dulling of these colours is known as the "opening of the eye of the button."

Remove the cupel from the muffle, and allow it to cool (*Note*); then the globule of silver suddenly glows and solidifies. Detach the bead and clean it with a hard brush. Weigh the bead carefully on a very delicate balance, and calculate the weight of silver present in the lead, stating the result in ounces troy per ton of lead.

In exact analysis, repeat the cupellation, running the assay against a



blank consisting of a similar weight of silver-free lead to which a piece of silver foil of suitable and known weight has been added.

**Silver in Silver Plate.** Silver plate usually contains about 92.5 per cent. of silver, the remainder being copper. Weigh out very accurately, preferably by the method of "swings," about 0.5 gm. of the plate, and wrap it in 2.5 to 3 gm. of silver-free lead foil. The foil should be folded as a filter-paper is folded, the plate dropped in, and a neat, compact packet made which can be dropped into the hot cupel quite easily.

Calculate the probable weight of silver and copper in the sample, assuming that the plate contains 92.5 per cent. of silver, and weigh out these quantities of the pure metals for a blank. Wrap them in a piece of lead foil equal in weight to that used in the assay.

Meanwhile the cupels should have been brushed to remove dust and should be heating in the muffle. When they are hot enough, drop the assay and the blank into two cupels placed side by side and burn off the lead. The lead oxide carries the copper with it into the cupel. The correct temperature can only be learned by experience; it is almost as bad to have it too high as too low. Ideally the furnace should be very hot at the start, should be cooled very considerably when the lead is burning, and should be raised just above the melting-point of silver ( $960^{\circ}\text{C.}$ ) at the end.

When "the eyes of the buttons have opened," the cupels are withdrawn from the furnace and are covered at once with other red-hot, cupels. Thus the silver cools slowly. Molten silver absorbs oxygen, which is given off when the metal cools. If the cooling is fast, this may shatter the button; the silver "spits." When the cupels are quite cold, the beads are detached, squeezed in the jaws of a pair of pliers to detach any bone ash, brushed with a hard brush, and weighed under the same conditions as the original metals were weighed.

The blank will be found to have lost a little silver. It is easy to calculate from this loss how much silver the plate will have lost, and therefore how much silver was originally present in the plate. Express the fineness of the plate in parts per thousand.

### Dry Assay of Gold Quartz

Since the amount of gold in gold ores rarely exceeds 2 ounces per ton, and is usually much less than this, it is necessary to extract the metal with great care. The process is divided into three parts.

- (1) The ore is heated with lead oxide and a flux, and the lead thus produced extracts the gold and silver from the ore.
- (2) The lead button is cupelled, and the silver and gold are left on the cupel.
- (3) The gold is "parted" from the silver by dissolving out the latter with nitric acid.

**Concentration of the Gold.** Powder the ore and pass it through a fine sieve. Nothing coarser than a B.S. 100-sieve should be used, and in the case of non-uniform ores it will be necessary to use a 210-mesh. Weigh out 50 gm. of the powdered ore, or 100 gm. if the ore is a poor one, or 32.67 gm. for one "assay ton" and mix this intimately with the flux.

The composition of a suitable flux for each of the three stated quantities of ore is given below in grammes.

Quartz ore . . . .	50	100	32.67
Red lead . . . .	40	40	30
$\text{Na}_2\text{CO}_3$ . . . .	75	125	40
Borax . . . .	15	25	10
Flour . . . .	4.5	4.5	4.5
Charcoal . . . .	1.5	1.5	1.5

Glass powder may also be added during the mixing, if it is necessary to increase the fluidity of the melt before "pouring."

Transfer the mixture to a smooth fireclay crucible, which is then covered with a lid and heated in a wind-furnace. The heat at first must not be too great, but must be raised considerably before "pouring." The lead oxide in the charge is reduced and the small globules of lead fall through the melt, collecting the gold in their passage. When the reaction is complete the crucible is drawn, swung and tapped, and the charge is poured into a conical iron mould. Detach the lead button from the glass-like slag, which should separate easily and must contain no particles of lead. The slag should be a clear fluid and resemble inferior bottle glass. If it is not satisfactory, repeat the assay, changing the temperature and the charge.

The slag from rich ores may contain particles of lead: if this is the case the slag should be crushed and mixed with 20 parts of red lead, 5 of  $\text{Na}_2\text{CO}_3$ , and 1 of charcoal, and heated once more. The lead button thus obtained is added to the first.

**Cupellation.** The lead button is scorified and cupelled, a high temperature being used so as to separate the copper completely. A high temperature may be used safely, since gold is much less volatile than silver. The button of gold and silver is then cleaned and weighed.

**Parting** consists of dissolving out the silver from the gold by nitric acid.

If the bead is yellow, it contains more than 50 per cent. of gold. If it contains more than 30 per cent. of gold, the gold will retain silver after the parting: but if not more than 30 per cent. of gold is present, the whole of the silver will be dissolved. The presence of too much silver causes the gold to be left as a powder which is difficult to manipulate. The most convenient proportions are 2.5 parts of silver to 1 part of gold.

If the gold does not exceed 30 per cent., flatten out the bead by hammering it carefully. If the bead is large, anneal it occasionally by heating it to redness on charcoal in the blowpipe-flame. In any case, anneal the flattened button before "parting" it.

Now heat a little concentrated nitric acid, diluted with its own volume of water, nearly to boiling in a tube, and drop the weighed button into it. Keep the liquid at this temperature for ten minutes. Then pour off the acid, and heat the button with nitric acid diluted with half its volume of water. Boil for several minutes, pour off the acid, and wash the residue with distilled water. Fill up the tube with water, cover the open end with a small porcelain crucible and quickly invert the tube, carefully avoiding loss. The gold will settle down in the bottom of the crucible. Remove the tube, and drain off the water from the crucible. As the surge of water

caused by the removal of the tube may wash some of the gold out of the crucible, it is best to put the crucible in water in a basin in such a way that its top edge is about an inch below the surface of the water before taking away the tube. If the tube is lifted upwards and sideways, the rush of water will be avoided.

Dry the gold, and heat it until it changes in colour from a dark red to yellow. Cool the metal, transfer it directly to the pan of a very delicate balance, and weigh it accurately. From this result calculate the weight of gold present in the ore, stating the result in ounces per ton.

If the button contains more than 30 per cent. of gold before "parting," it will retain silver. In such a case sufficient silver is added to raise the proportions to 2.5 parts of silver to 1 part of gold by cupelling the button with the necessary quantity of silver and a small piece of lead foil, and the "parting" is repeated with this alloy.

If the gold weighs only 2 or 3 milligrams, the requisite quantity of silver may be alloyed with it by simple fusion on a clean cupel over the blowpipe. The silver which is introduced in the red lead, or in the metallic lead, must be determined and allowance made for it.

**Example of Gold-ore Assay.** 50 gm. of ore were fused with flux, and a lead

$$\text{The weight of gold} = \frac{2240 \times 7000 \times 0.001}{50} = 313.6 \text{ grains per ton of ore.}$$

$$= \frac{313.6}{480} = 0.65 \text{ ounce per ton of ore.}$$

From the above results, the weight of Ag in the button = 3.5 milligrams.

Subtracting the weight of Ag in the red lead  $\frac{1.1}{2.0}$  } = 3.1 "   
 and the weight of Ag added, . . . . .

the weight of silver from the ore = 0.4 "

Therefore by calculation from this result, as above :

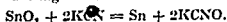
The weight of silver = 0.26 ounce per ton of ore.

### Dry Assay of Tin Ores

Cassiterite, "tinstone," or "black tin" is the ordinary tin ore of commerce. This mineral consists mainly of  $\text{SnO}_2$ . It may be assayed as described below if it is fairly free from quartz and other "gangue," and if it contains not less than 60 per cent. of metallic tin.

A suitable charge may be 20 grm. of the mineral, 40 grm. of potassium cyanide and 1 grm. of powdered charcoal. A small quantity of the cyanide is placed at the bottom of a small clay crucible. The ore, most of the remaining cyanide, and the carbon are intimately mixed on a sheet of paper and added. The paper is washed off with the reserved cyanide, and the residues are added as a seal to the contents of the crucible.

The crucible is placed in a wind-furnace and heated at a low red heat for twenty minutes. During this time the oxide is reduced.



The tin is present as small globules in the slag. These globules must be collected by raising the temperature considerably for a short time before pouring. The crucible is then drawn, swung and tapped fairly vigorously, and the molten charge is poured into a cold button-mould.

When quite cold, the salts are removed from the tin by placing the button under a running tap in a sink. The tin is dried and weighed.

The dry assay generally gives results slightly lower than those given by the wet assay. The loss of tin is considerable, but there is a compensating gain of iron. If desired, the percentage of tin in the button may be determined by dissolving a piece of it in hydrochloric acid and determining the tin iodometrically (p. 165).

Certain samples of cassiterite cannot be assayed directly in this manner. They do not give buttons, but merely irregular metallic masses. Such ores may sometimes be assayed if they are first cleaned as follows: A known weight, say 20 grm., of the finely-divided ore is digested with 30 ml. of concentrated hydrochloric acid for half an hour at a temperature not far short of boiling. Then 5 ml. of concentrated nitric acid are added and the liquid is boiled for ten minutes.

The cold liquid is diluted and stirred, and the residual tinstone is washed several times by decantation with hot water followed by decantation with dilute ammonia. It is then transferred to a filter-paper, washed and dried. The tin is determined by the dry assay as described above. The filter-paper may be added to the charge in the crucible.

*Note.* As the determination of tin by the dry assay may sometimes be unreliable, in commercial practice the ore is frequently opened up by fusion with sodium hydroxide or sodium peroxide, and the tin is determined volumetrically by the bromate process (p. 183).

caused by the removal of the tube may wash some of the gold out of the crucible, it is best to put the crucible in water in a basin in such a way that its top edge is about an inch below the surface of the water before taking away the tube. If the tube is lifted upwards and sideways, the rush of water will be avoided.

Dry the gold, and heat it until it changes in colour from a dark red to yellow. Cool the metal, transfer it directly to the pan of a very delicate balance, and weigh it accurately. From this result calculate the weight of gold present in the ore, stating the result in ounces per ton.

If the button contains more than 30 per cent. of gold before "parting," it will retain silver. In such a case sufficient silver is added to raise the proportions to 2.5 parts of silver to 1 part of gold by cupelling the button with the necessary quantity of silver and a small piece of lead foil, and the "parting" is repeated with this alloy.

If the gold weighs only 2 or 3 milligrams, the requisite quantity of silver may be alloyed with it by simple fusion on a clean cupel over the blowpipe. The silver which is introduced in the red lead, or in the metallic lead, must be determined and allowance made for it.

*Example of Gold-ore Assay.* 50 gm. of ore were fused with flux and 2 lead

$$\text{The weight of gold} = \frac{2240 \times 7000 \times 0.001}{50} = 313.6 \text{ grains per ton of ore.}$$

$$= \frac{313.6}{480} = 0.65 \text{ ounce per ton of ore.}$$

From the above results, the weight of Ag in the button = 3.5 milligrams.

Subtracting the weight of Ag in the red lead . 1.1  
and the weight of Ag added, . 2.0 } = 3.1 "

the weight of silver from the ore = 0.4 "

Therefore by calculation from this result, as above :

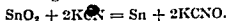
The weight of silver = 0.26 ounce per ton of ore.

### Dry Assay of Tin Ores

Cassiterite, "tinstone," or "black tin" is the ordinary tin ore of commerce. This mineral consists mainly of  $\text{SnO}_2$ . It may be assayed as described below if it is fairly free from quartz and other "gangue," and if it contains not less than 60 per cent. of metallic tin.

A suitable charge may be 20 grm. of the mineral, 40 grm. of potassium cyanide and 1 grm. of powdered charcoal. A small quantity of the cyanide is placed at the bottom of a small clay crucible. The ore, most of the remaining cyanide, and the carbon are intimately mixed on a sheet of paper and added. The paper is washed off with the reserved cyanide, and the residues are added as a seal to the contents of the crucible.

The crucible is placed in a wind-furnace and heated at a low red heat for twenty minutes. During this time the oxide is reduced.



The tin is present as small globules in the slag. These globules must be collected by raising the temperature considerably for a short time before pouring. The crucible is then drawn, swung and tapped fairly vigorously, and the molten charge is poured into a cold button-mould.

When quite cold, the salts are removed from the tin by placing the button under a running tap in a sink. The tin is dried and weighed.

The dry assay generally gives results slightly lower than those given by the wet assay. The loss of tin is considerable, but there is a compensating gain of iron. If desired, the percentage of tin in the button may be determined by dissolving a piece of it in hydrochloric acid and determining the tin iodometrically (p. 165).

Certain samples of cassiterite cannot be assayed directly in this manner. They do not give buttons, but merely irregular metallic masses. Such ores may sometimes be assayed if they are first cleaned as follows: A known weight, say 20 grm., of the finely-divided ore is digested with 30 ml. of concentrated hydrochloric acid for half an hour at a temperature not far short of boiling. Then 5 ml. of concentrated nitric acid are added and the liquid is boiled for ten minutes.

The cold liquid is diluted and stirred, and the residual tinstone is washed several times by decantation with hot water followed by decantation with dilute ammonia. It is then transferred to a filter-paper, washed and dried. The tin is determined by the dry assay as described above. The filter-paper may be added to the charge in the crucible.

*Note.* As the determination of tin by the dry assay may sometimes be unreliable, in commercial practice the ore is frequently opened up by fusion with sodium hydroxide or sodium peroxide, and the tin is determined volumetrically by the bromate process (p. 183).

## SECTION XI

### WATER ANALYSIS

#### Collection and Inspection of the Sample

SAMPLES of water are most conveniently collected and stored in Winchester quart bottles. These bottles are made of good quality glass and are provided with accurately fitting stoppers. Each bottle holds about 2400 ml. For an ordinary analysis one Winchester quart bottle filled with the water will be found sufficient.

Before the bottle is filled with the sample, it should be washed out thoroughly with water and then allowed to drain in an inverted position. Bottles which have been used for acids are to be preferred because they are most easily cleaned. The use of stoneware bottles and of corks in storing water-samples is to be condemned.

Before the bottles are filled, they should be rinsed out two or three times with the water. When the water is to be collected from a river or spring the bottle is totally immersed in the water, and is filled to within  $\frac{1}{2}$  inch of the bottom of the stopper. If the water is supplied from a pump or tap, several gallons should be allowed to flow away before the sample is taken. A sample of a town supply must be drawn direct from the street-mains, and not from a storage cistern.

The stopper is inserted as soon as the bottle has been filled. It should be held in position by drawing down tightly over it a piece of sheet rubber, or of clean calico or linen rag, the edges of which are firmly tied round just beneath the projecting edge of the neck with string or with thin copper binding-wire. The fastening should be sealed with sealing-wax. No lute or other material, which might find its way into the bottle when the stopper is removed, must be employed. Immediately the sample has been taken a label describing the sample, and stating the date, time and place of sampling should be affixed to the bottle.

Samples of water should be stored in a cold, dark room or cellar.

**Order of Work.** In carrying out the following determinations, the order in which they are to be started should be carefully considered, with a view to the greatest possible economy of time and the minimum change in properties of the sample. Ammonia, organic matter and dissolved oxygen should be determined as soon as possible after the sample has been collected, and immediately after the bottle has been opened, since these constituents undergo rapid changes in amount when the water is kept or is exposed to the air. Unless stated otherwise below, the water in the bottle should be mixed by shaking before any portion is poured off for analysis.

It is usually unnecessary to carry out the whole of the following determinations on any one sample of water, and the following scheme indicates the more important data required for waters for various purposes :

**Raw and Softened Boiler-Feed Waters.** Total, suspended and organic solids, hardness,  $P$ , alkalinity (or acidity), sulphates, chlorides, carbon dioxide, silica, dissolved oxygen. A detailed analysis of the inorganic solids may be necessary in the first instance, and at occasional intervals.

**Condensate.** Dissolved oxygen,  $P$ , alkalinity, hardness, chlorides.

**Water from Boilers.** Alkalinity,  $P_n$ , phosphates, sulphates, silica, sodium, chlorides.

**Condenser Cooling Water.** Chlorine (if chlorinated), chlorides.

**Drinking Waters.** Oxygen absorption, suspended solids, chlorides, free and saline and albuminoid ammonias, nitrites, nitrates, poisonous metals,  $P_n$ , free chlorine (if chlorinated).

**Effluents.** Biological oxygen demand, suspended solids, free and saline and albuminoid ammonias,  $P_n$ , temperature.

The **Colour of the Water** is observed by pouring it into a 100-ml. Nessler tube, and looking down the tube at a white surface, placed so that light is reflected up through the column of liquid. If a numerical measurement of the colour is required, this can be made by means of a Lovibond tintometer; or by determining the number of ml. of a 0.0025 per cent. solution of Bismarck brown which, on dilution to 1 litre, match the shade of the water. The value so obtained is about 10 per cent. of the Lovibond value.

The **Taste and Smell** of the water are usually observed after it has been gently heated.

**Acidity.** Pure natural water is usually slightly alkaline in reaction, and a strip of neutral litmus-paper immersed in it for thirty minutes becomes distinctly blue. A decidedly acid reaction usually indicates the presence in the water of manufacturers' waste or of mine-products, but water derived from peat and heath-land is also slightly acid.

The "acidity" is best expressed in terms of hydrogen-ion concentration. This may be measured colorimetrically (p. 206).

### Examination of the Suspended Matter

**Chemical Examination of the Suspended Matter.** The presence of suspended matter in water usually indicates imperfect filtration, but it may arise from the action of the water on lead (p. 367), and to other causes. It is not usual to filter the water before analysis unless it is very turbid. If, however, much suspended matter is present, its amount must be determined, and the water may at the same time be rendered clear, as follows:

Filter 100 ml. to 1 litre of water, according to the amount of suspended matter present, through a tared paper on a weighed Gooch crucible containing a pad of asbestos 2 mm. thick, dried at 105° C. Dry the filter and its contents to constant weight at 105° C. This gives the total suspended matter. It should be expressed in parts per 100,000, the temperature of drying also being recorded.

The residue is then ignited (p. 79), cooled and weighed, the result giving the inorganic suspended matter.

If a filter-paper is used, this should not be wetted before or washed after the filtration. The first 50 ml. of the filtrate should be rejected.

**Microscopic Examination of the Suspended Matter.** Allow the water to remain in a tall cylinder for several hours, until the suspended matter has been deposited. Carefully pour off the clear supernatant water as completely as possible; then transfer a drop of the residual liquid to a glass



slide, and examine it under a one-sixth objective. Take special care to look for fibres of wool, hair, muscular tissue, or any kind of animal matter which would be indicative of sewage. The presence of organisms should be carefully noted, and also the presence of chlorophyll granules, growths and cells, which will indicate vegetable matter. Potable waters should be free from all visible suspended matter, dead or alive, but for the identification of the objects seen and the interpretation of the results the references on p. 246 should be consulted. It should be remembered, too, that a satisfactory chemical and microscopical analysis is not necessarily a guarantee that the water is free from harmful bacteria, since these are invisible under ordinary magnifications; and that with drinking waters a biological test is always desirable.

### Total Dissolved Solids

Rinse a clean platinum or nickel evaporating-dish with distilled water, heat it in a steam-oven, allow it to cool for ten minutes in a desiccator and weigh it carefully. Place the dish on a glass ring on a water-bath, or on a beaker of suitable size placed on a tripod stand. The bath or beaker should be about two-thirds filled with water, and, if a beaker is used, a few small pieces of pumice should be placed in it to prevent bumping. Measure 500 ml. of the sample in a graduated delivering flask, and fill the dish within about 1 cm. from its edge with the water, filtering the sample if necessary. The volume of the water used may be reduced if much dissolved solid matter is present. As the liquid evaporates, add more of the sample, until the whole of it has been transferred to the dish. When all the water has evaporated, dry the outside of the dish, place it in the steam-oven, and heat it at  $110^{\circ}\text{C}$ . until its weight is constant, cooling it in a desiccator for ten minutes before weighing.

If the residue in the dish is very hygroscopic, the actual weighing must be performed rapidly. It may even prove convenient to weigh the solids slightly warm, and this may be done so long as the empty dish is weighed in the same way. With a little practice it will be found possible to do this with sufficient accuracy, and it is usual to judge the temperature of the dish by holding it with tongs and allowing it to touch the back of the hand. Weighings should be carried out to the nearest milligram, and in recording the results a note should be made of the temperature at which the solids were dried.

Then ignite the residue at a low red heat, noting the changes that occur in the colour and odour. Cool in a desiccator and reweigh. The difference in weight gives the loss on ignition. This loss is some indication of the amount of organic matter present.

### Free and Saline Ammonia

This determination must be conducted in a room which contains no ammonium salts or other sources of ammonia, and it should be made as

soon as possible after the collection of the sample, and immediately after the bottle has been opened. It is a good plan, when first opening the bottle, to shake it so that a little of the water splashes over the lip of the neck and so washes off any traces of impurities that may have lodged on it.

The method depends on the fact that when the water is distilled with a little sodium carbonate the whole of the ammonia, which is present in the water either in the free or in the combined state, passes over in the first portion of the distillate and may be determined by the addition of Nessler solution, which gives a yellow or brown coloration with ammonia or ammonium salts (see p. 246). This colour is matched by adding the same quantity of the Nessler solution to the same volume of pure water, to which a suitable and known volume of standard ammonium chloride solution has been added.

**Nessler Solution.** Threelitres of this solution may be prepared according to the following directions, but a smaller volume will usually suffice, and may be made from proportionately smaller quantities of materials.

Dissolve 180 grm. of potassium iodide in 250 ml. of water and pour this solution upon 70 grm. of mercuric chloride contained in a glazed porcelain mortar; then triturate the mixture until the solid matter has dissolved, and make up the whole to 2500 ml. by the addition of water. Now add 454 grm. of potassium hydroxide in sticks, allow the solids to dissolve, and, when the liquid has cooled, add a saturated solution of mercuric chloride gradually and in sufficient quantity to form a slight permanent precipitate. Dilute this solution to 3 litres, allow it to stand, and then carefully decant the clear liquid.

Keep this Nessler solution in bottles which are closed with well-fitting rubber stoppers, and decant a portion of the clear solution from time to time into a smaller bottle for use. A glass tube, with a 2-ml. mark on it is used to measure out and deliver the required volume of the solution.

**Standard Ammonium Chloride Solution.** Weigh out accurately 3.15 grm. of pure ammonium chloride, dissolve in water, and make up the solution to 1 litre. This solution is too concentrated for use, but it makes a convenient stock solution. When the standard solution is required, dilute 10 ml. of the stock solution to 1 litre. Each millilitre of the diluted solution corresponds with 0.01 milligram of  $\text{NH}_3$ .

**Water Free from Ammonia.** Ordinary distilled or soft water frequently contains sufficient ammonia to make it unfit for use in the determination of ammonia. In order to determine whether ammonia is present, a 50-ml. Nessler tube is filled to the mark with the distilled water, and 2 ml. of Nessler solution are added. The tube is then placed on a white surface, and if no yellow coloration appears after standing for five minutes the water is sufficiently pure for use.

If, however, a yellow or brown coloration appears, re-distil the water in the following way: Pour the water into a large flask, and add a little potassium permanganate and about 1 grm. of freshly-ignited sodium carbonate crystals. Connect the flask with a condenser, and then boil the water. After rejecting the first portion of the distillate, collect the remainder in a Nessler tube and test it with Nessler solution as described.

As soon as the distillate ceases to give a coloration with Nessler solution, collect it in a clean Winchester quart bottle, and keep the tightly-stoppered bottle in a room which contains no ammonium salts or other sources of ammonia.

contact of the steam with rubber is thus prevented.

**Procedure.** The following preliminary test determines the volume of water to be used: To 50 ml. of the water-sample in a Nessler tube on a white tile are added 2 ml. of Nessler solution, and the mixture is stirred. Fifty millilitres of the distilled water, free from ammonia, are poured into a second tube, and 0.5 ml. of the dilute standard ammonium chloride solution and 2 ml. of Nessler solution are added.

If, after the cylinders have been allowed to stand for about five minutes, the intensity of colour in both is about the same, 500 ml. of the water is a suitable volume to be taken. If the coloration produced by the water-sample is less or greater than that of the standard, a proportionately larger or smaller quantity of the water must be used. After a little experience it is possible to judge this quantity by simple inspection. The coloration which corresponds with that given by about 2 ml. of the standard ammonium chloride solution, is most suitable for the accurate determination of ammonia by this method.

(a) *Process of Distillation.* Connect the distillation flask to the condenser, and free the apparatus from ammonia as follows: Pour into the flask about 500 ml. of water free from ammonia, and add 1 grm. of freshly-ignited sodium carbonate, with a few pieces of ignited pumice to prevent bumping. Heat the flask with an Argand burner, or with a Bunsen burner which is raised to within 1 cm. from the bottom of the flask so as to flatten out the flame.

If a Liebig condenser is being used, allow the steam to blow through the whole apparatus for a few minutes, until about 50 ml. of distillate collect. Test this for ammonia by adding 2 ml. of the Nessler solution. If any coloration is seen, distil over about 50 ml. more of the water into a Nessler tube and test again. Continue this procedure until 50 ml. of the distillate give no coloration with Nessler solution.

Pour the requisite quantity of the water under examination into the flask, and distil over one 100-ml. portion. Mix this by pouring it into another cylinder and match 50 ml. of it as is described below. If the amount of ammonia present is such as to produce too deep a colour for matching conveniently, dilute the solution until a suitable colour is obtained, and match roughly. Then use the other 50 ml. to obtain a more exact match.

In the meantime another 100 ml. should have been collected, and this is treated similarly; normally the 50 ml. taken will not require dilution. Collect another 50 ml. of distillate, and determine the ammonia present; if

this corresponds with 1.0 ml. of standard or less the distillation may be regarded as finished. If it is more collect one more 50-ml. portion, and then conclude the distillation, even if the volume of standard required to match it exceeds 1.0 ml.

Allow the apparatus and its contents to stand by undisturbed for the subsequent determination of the "albuminoid ammonia" (see below).

(b) *Process of "Nesslerising."* Add 2 ml. of Nessler solution to the contents of the tube which contains the distillate, stir well, and place the tube on a white tile. Now make a comparison-test by dropping into another Nessler tube 1 ml. of the standard ammonium chloride solution from a burette, adding 49 ml. of ammonia-free water and 2 ml. of Nessler solution, and mixing the liquids by stirring. Allow both tubes to stand for five minutes before comparing the tints.

If the intensity of colour in the two tubes is not the same, throw away the contents of the comparison-tube and rinse it out with water. Add more or less of the ammonium chloride solution, as may be considered necessary, and dilute with ammonia-free water to the 50-ml. mark. Mix the liquid with 2 ml. of Nessler solution, allow the tube to stand for five minutes, and compare the coloration with that in the tube under test.

These operations are repeated until the colour in the tube under test matches that in the comparison-tube. The volume of the ammonium chloride solution which has been required is noted. The process may usually be hastened by preparing four standard Nessler tubes containing 0.5, 1, 2 and 3 ml., respectively, of the ammonium chloride solution, and comparing the intensity of the colour of the tube under test with these.

The addition of the ammonium chloride solution to the water must always precede that of the Nessler solution; otherwise the liquid will become turbid and an accurate comparison of the colours will be impossible.

The separate volumes of ammonium chloride required by the different portions of the distillate are added together, and from this the weight of ammonia contained in 100,000 parts of the water is found.

**Example.** Set out the result as follows :—

Volume collected	Volume taken.	Volume after dilution	Volume of standard to match 50 ml of diluted distillate	Volume of standard to match total distillate
100	50	100	1.5	6.0 ml.
100	50	50	1.2	2.4
50	50	50	1.1	1.1
50	50	50	0.9	0.9
Total				10.4

Thus, 500 grm. of water contained 0.000104 grm. of  $\text{NH}_3$  = 0.0208 part of  $\text{NH}_3$  per 100,000.

### Albuminoid Ammonia

When an organic substance containing nitrogen is mixed with an alkaline solution of potassium permanganate and the liquid is boiled, either a

out side by side with the samples, the bottle containing this water being allowed to stand for four hours at 80° F. The titration figure obtained is in effect a standardisation of the thiosulphate against the permanganate, under the conditions of the experiment.

**Calculation.** Let  $x$  represent the number of millilitres of thiosulphate solution which have been used in the titration of the permanganate in the distilled water, and  $y$  the number of millilitres used in the titration of the permanganate in the water under examination. Then  $(x - y)$  is the number of millilitres of thiosulphate solution which are equivalent to the permanganate reduced by the water.

Further, if the amount of available oxygen in the 10 ml. of permanganate originally added is represented by  $a$ , then the weight of oxygen required to oxidise the organic matter in 250 ml. of the water will be

$$\frac{(x - y)a}{x}$$

But  $a = 0.001$  gram. of oxygen, and therefore the amount of oxygen consumed by 100,000 parts of the water

$$= \frac{(x - y) \times 0.001 \times 100,000}{x \times 250} = \frac{(x - y)0.4}{x}$$

**Example.** In a particular determination, 12.5 ml. of the standard thiosulphate solution were required for the distilled water, and 10 ml. for the water under examination. The amount of oxygen consumed by 100,000 parts would accordingly be in this case

$$\frac{(12.5 - 10)0.4}{12.5} = 0.08.$$

### Chlorides and Chlorine

**Chlorine present as Chloride.** Chlorine is usually present in the form of sodium chloride, and it is frequently reported in terms of that salt. The method is described on p. 193, a standard solution of silver nitrate being added to the water, with potassium chromate solution as indicator. The solutions required are :

(a) *Standard Solution of Silver Nitrate.* Dissolve 4.791 gram. of pure silver nitrate in distilled water, and make up the solution to 1 litre. The solution should be standardised against a solution of pure sodium chloride containing 1.648 gram. per litre. If 100 ml. of water are used in the titration, 1 ml. of this silver nitrate solution will represent 1 part of chlorine per 100,000 of the water.

(b) *Solution of Potassium Chromate.* Dissolve 1 part of neutral potassium chromate in 20 parts of water. The chromate solution must be freed from any chloride by adding a solution of silver nitrate until a permanent red precipitate is just obtained, and then filtering the liquid.

**Procedure.** Pour the silver nitrate solution (a) into a burette. Measure 100 ml. of the water into a porcelain dish, and add 1 ml. of the potassium chromate solution (b): Add the silver nitrate solution, cautiously, until a faint, but permanent, red colour is just imparted to the liquid.

It will be found convenient, until experience has been gained, to prepare

a similar dish containing 100 ml. of water mixed with 1 ml. of the potassium chromate solution, to which silver nitrate solution has been added, but not in excess. If the two dishes are placed side by side, the faintest appearance of a reddish tint in the test-dish will then be easily seen.

A blank experiment is made by finding the volume of the silver solution required to give the same reddish tint to a mixture of 1 ml. of the chromate with 100 ml. of distilled water. The number of millilitres of the silver nitrate solution required by the water used, less the volume required by the blank, gives the chlorine (present as chloride) in parts per 100,000 of the water.

*Note.* The volume of water to be used in the test is dependent upon the amount of chloride present. The method is not suitable for waters containing less than 0.5 part or more than 100 parts of chloride per 100,000 of water.

**Free Chlorine.** Water is frequently sterilised by chlorine both for drinking purposes and for use in swimming baths, etc. If nitrites, which also give a colour with the reagent, are absent, free chlorine may be determined by means of orthotolidine.

The following solutions are required :

(a) One gramme of orthotolidine is dissolved in dilute hydrochloric acid, and the solution made up to 1 litre.

(b) A solution of copper sulphate containing 3 grm. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and 2 ml. of concentrated sulphuric acid made up to 200 ml. with water.

(c) A solution of 0.05 grm. of potassium dichromate in 200 ml. of water con-

similar to the standard solution. The standard solution is prepared by dissolving different volumes of soluble shows the volumes with various concentra-

Chlorine, parts per million.	Ml of reagent diluted to 100 ml		Chlorine, parts per million	Ml of reagent diluted to 100 ml.	
	$\text{CuSO}_4$	$\text{K}_2\text{Cr}_2\text{O}_7$		$\text{CuSO}_4$	$\text{K}_2\text{Cr}_2\text{O}_7$
0.02	0.0	2.1	0.20	1.0	20.0
0.04	0.0	4.3	0.30	1.0	30.0
0.06	0.8	6.6	0.40	2.0	38.0
0.08	1.5	8.7	0.50	2.0	45.0
0.10	1.8	10.0	0.80	2.0	63.0

### Nitrite

**Determination of Nitrite Colorimetrically.** This method, that of Griess-Ilosva, is used for very small amounts of nitrites (of the order of 0.01 to 0.0005 part per 100,000). It depends on the formation of an intensely-coloured azo dye which imparts a red coloration to the water, and should be carried out on a fresh sample of water, since the nitrite is converted into nitrate or ammonia by bacterial action when the sample is allowed to stand. The following solutions are required :

(a) Dissolve 1 grm. of sulphanilic acid in a mixture of 10 ml. of glacial

Clark's method is the older; it does not yield accurate results if a large quantity of magnesium salts is present, but it has the advantage that it actually measures the soap-consuming power of the water. The titration method gives better results on the whole, since the magnesium salts are also precipitated quantitatively (p. 365).

### Hardness by Soap Solution (Clark's Method)

This method depends on the fact that when a solution of soap is mixed with solution of a calcium or magnesium salt, an insoluble calcium or magnesium soap is produced. Accordingly, if the water is titrated with the soap solution no lather will form on shaking until the soap solution is in excess.

The solution of soap in methylated spirit, which is used in this process, is first standardised against a solution of calcium chloride of known concentration. The water is titrated against this standard soap solution, and according to British usage the number of "degrees of hardness" of the water is obtained from the volume of soap solution used. Each degree of hardness corresponds with 1 part of  $\text{CaCO}_3$  per 100,000 of water.

The following solutions are required :

(a) *Standard Solution of Calcium Chloride.* Weigh accurately 0.2 gm. of pure Iceland spar, and dissolve it in dilute hydrochloric acid, taking care to keep the vessel covered to prevent loss by spirting. Evaporate this solution to dryness on a water-bath; then add water and again evaporate to dryness, and repeat these processes, *once* at least, in order to remove all free hydrochloric acid. Dissolve the residue of neutral calcium chloride in water, and make up the solution to 1 litre.

(b) *Preparation of Soap Solution.* Potassium oleate soap is prepared by rubbing in a mortar 150 parts of lead plaster (*Emplastrum Plumbi*, B.P.) with 40 parts of dry potassium carbonate. When these substances have been thoroughly mixed, a little methylated spirit is added and the process of mixture in the mortar is continued until a creamy mass is formed. This is stirred with more spirit, and the liquid is decanted after the sediment has settled. The solution is made up to 1 litre with methylated spirit diluted with half its volume of water.

Another Method of Preparing the Soap Solution is to dissolve 80 gm. of

in order to give the concentration of soap required.

*Standardisation of Soap Solution.* The soap solution must be diluted until 14.25 ml. of it just produce a permanent lather when shaken with 50 ml. of the standard calcium chloride solution.

Measure 50 ml. of the calcium chloride solution (a) into a stoppered bottle of 250 ml. capacity. Now allow 1 ml. of the soap solution to flow from a burette into the bottle, and close the bottle and shake it vigorously for a short time. If no permanent lather is produced, add another millilitre of the solution and shake again. Continue the addition of the soap, shaking the water well after each addition, until a lather is formed which

remains for a short time when the bottle is laid upon its side on the bench. The titration is finished when the lather remains upon the surface in an unbroken layer for five minutes. Towards the end of the titration, the volume of soap solution which is added each time should be lessened, and it should finally not exceed 0.2 ml. Experience renders it possible to detect the approach of the end of the reaction by the sound and sensation produced during shaking, because the sound and shock become much more gentle when a lather begins to form.

The soap solution can now be diluted by the calculated volume of water-alcohol mixture to a concentration such that exactly 14.25 ml. of it are required to produce the lather with 50 ml. of the calcium chloride solution. The concentration of the soap solution should be checked after it has been allowed to stand for twenty-four hours, because a sediment usually forms which reduces its strength. It is on this account preferable to defer the final dilution and titration of the solution until no further sediment is deposited.

**Total Hardness.** Measure 50 ml. of the water into a stoppered bottle of 250 ml. capacity. Shake the water well, and remove any carbon dioxide, which has been evolved, by sucking out the air from the upper part of the bottle by means of a pipette; repeat these processes once at least (*Note*). Then titrate the water with the standard soap solution in the way described above. If more than 16 ml. of soap solution are required, dilute a suitable measured volume of the sample to 50 ml. with boiled, distilled water (*Note*) and titrate again.

The number of degrees of hardness in the water, expressed as parts of calcium carbonate per 100,000, may now be obtained from the number of millilitres of soap solution used, by reference to the Hardness Table (see below).

If much magnesium salt is present, it will be difficult to determine the end-point. This is due partly to the formation of a permanent scum upon the water, but also to the fact that the soap solution acts much more slowly upon magnesium salts than it does upon calcium salts. When magnesium salts are present, it is best to dilute the water until not more than 7 ml. of the soap solution are required for the titration, and the bottle should be allowed to stand for at least ten minutes after the titration has been finished to make certain that the lather is permanent.

*Note.* Carbon dioxide acts on soap solution in such a way as to prevent it from giving a lather. Hence, all distilled water used for dilution or for making solutions, should be freshly boiled and cooled quickly.

**Permanent Hardness.** The method consists in boiling the water until any salts, which are precipitated by boiling, are thrown out of solution. The liquid is then made up to its original volume with air-free distilled water, and is filtered at once. The hardness is determined in the clear filtrate.

Measure about 250 ml. of the sample into a flask, and weigh the flask and contents. Boil gently for half an hour, adding boiled distilled water from time to time, to replace that which evaporates. Cool quickly, and make up the flask and its contents to their original weight (*Note*) with cold, recently boiled, distilled water. Mix well, pour through a dry filter, reject



the first 50 ml. of filtrate and titrate a suitable volume of the filtrate with soap solution.

The degrees of Permanent Hardness are then obtained by reference to the Hardness Table.

*Note.* Instead of weighing the sample, an exactly measured volume of it may be taken, and the water may be made up to the same volume again after it has been boiled, filtered and cooled. In practice, however, this procedure is less rapid than weighing.

**Temporary Hardness.** The difference between the Total Hardness and the Permanent Hardness gives the Temporary Hardness of the water.

**HARDNESS TABLE**  
Parts of  $\text{CaCO}_3$  per 100,000

Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .	Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .	Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .	Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .	Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .	Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .	Ml. of Soap Solution.	Parts of $\text{CaCO}_3$ .
0.7	.00	3.3	3.64	5.9	7.29	8.5	11.05	11.1	15.00	13.7	19.13		
.8	.16	.4	.77	6.0	.43	.6	.20	.2	.16	.8	.29		
.9	.32	.5	.90	.1	.57	.7	.35	.3	.32	.9	.44		
1.0	.48	.6	4.03	.2	.71	.8	.50	.4	.48	14.0	.60		
.1	.63	.7	.16	.3	.86	.9	.65	.5	.63	.1	.76		
.2	.79	.8	.29	.4	8.00	9.0	.80	.6	.79	.2	.92		
.3	.95	.9	.43	.5	.14	.1	.95	.7	.95	.3	20.08		
.4	1.11	4.0	.57	.6	.29	.2	12.11	.8	16.11	.4	.24		
.5	.27	.1	.71	.7	.43	.3	.26	.9	.27	.5	.40		
.6	.43	.2	.86	.8	.57	.4	.41	12.0	.43	.6	.56		
.7	.56	.3	5.00	.9	.71	.5	.56	.1	.59	.7	.71		
.8	.69	.4	.14	7.0	.86	.6	.71	.2	.75	.8	.87		
.9	.82	.5	.29	.1	9.00	.7	.86	.3	.90	.9	21.03		
2.0	.95	.6	.43	.2	.14	.8	13.01	.4	17.06	15.0	.19		
.1	2.08	.7	.57	.3	.29	.9	.16	.5	.22	.1	.35		
.2	.21	.8	.71	.4	.43	10.0	.31	.6	.38	.2	.51		
.3	.34	.9	.86	.5	.57	.1	.46	.7	.54	.3	.68		
.4	.47	5.0	6.00	.6	.71	.2	.61	.8	.70	.4	.85		
.5	.60	.1	.14	.7	.86	.3	.76	.9	.86	.5	22.02		
.6	.73	.2	.29	.8	10.00	.4	.91	13.0	18.02	.6	.18		
.7	.86	.3	.43	.9	.15	.5	14.06	.1	.17	.7	.35		
.8	.99	.4	.57	8.0	.30	.6	.21	.2	.33	.8	.52		
.9	3.12	.5	.71	.1	.45	.7	.37	.3	.49	.9	.69		
3.0	.25	.6	.86	.2	.60	.8	.52	.4	.65	16.0	.86		
.1	.38	.7	7.00	.3	.75	.9	.68	.5	.81				
.2	.51	8	.14	.4	.90	11.0	.84	.6	.97				

the liquid is clear, titrating with a .5 per cent. solution of  $\text{HCl}$  in alcohol to a permanent pink colour. The solution is diluted to 1 litre with 90 per cent. alcohol, and standardised as follows:

(carbonate-free) to phenolphthalein, back-titrate with 0.1 N.  $\text{HNO}_3$ , adding 1 drop in excess, and then titrate with the palmitate reagent to a faint pink, correcting the titration by deducting 0.3 ml.; 100 ml. of the barium chloride solution = 5 ml. of 0.1 N. palmitate solution.

**Total Hardness.** Slightly acidify 100 ml. of the water with 0.1 N.  $\text{HNO}_3$ , to methyl orange, boil for three minutes with 1 drop of bromine water, cool, and proceed as in the standardisation. If  $a$  ml. is the corrected titration with a 0.1 N. palmitate solution, then the total hardness is equivalent to  $5a$  parts of  $\text{CaCO}_3$  per 100,000.

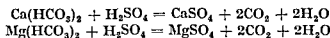
**Calcium Hardness.** Slightly acidify 100 ml. of water with 0.1 N.  $\text{HNO}_3$ , add

hardness is a  $5b$  parts of  $\text{CaCO}_3$  per 100,000.

**Magnesium Hardness.** This is the difference between the total and the calcium hardnesses.

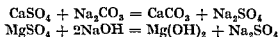
### Determination of Hardness by Standard Acid

The calcium and magnesium bicarbonates, which cause the temporary hardness, are first determined by titration of a portion of the water with standard acid. The reactions which occur are :



The amount of acid used is converted into its equivalent of  $\text{CaCO}_3$  (each millilitre of decinormal acid corresponds with 5 milligrams of  $\text{CaCO}_3$ ), and from this the "temporary" hardness is calculated as parts of  $\text{CaCO}_3$  per 100,000.

The soluble salts of calcium and magnesium are then removed from another portion of the water by adding a mixture of equal volumes of standard sodium hydroxide and sodium carbonate solutions in excess, and the excess is back titrated with standard acid. The reactions which occur are :

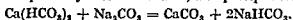


The sodium carbonate converts the calcium salts into  $\text{CaCO}_3$  and the sodium hydroxide precipitates the magnesium salts as  $\text{Mg}(\text{OH})_2$ . From the volume of alkali used, the weight of soluble salts of calcium and magnesium, expressed in terms of parts of  $\text{CaCO}_3$  per 100,000, is calculated, and this gives the "permanent" hardness.

**Temporary Hardness ("Alkalinity").** Add a few drops of methyl orange to 500 ml. of the water, or to a smaller volume if the water is very hard. Then add decinormal sulphuric acid from a burette until the end-point is reached. The end-point can best be obtained by adding the same amount of indicator to 500 ml. of distilled water and running in acid until the colour of the solution has changed to a faint red. This tint can then be matched against that of the water under examination. From the number of millilitres of acid used, less that required for the distilled water blank, the corresponding weight of  $\text{CaCO}_3$  is calculated, and this is converted into parts per 100,000.

**Permanent Hardness.** Boil 250 ml. of the water in a conical flask to expel most of the carbon dioxide. Add to it 50 ml. of a mixture of equal volumes of decinormal NaOH and decinormal  $\text{Na}_2\text{CO}_3$  and evaporate to about 100 ml. Cool the liquid, make it up to 250 ml. with boiled, distilled water, and allow the whole to stand until the calcium carbonate and magnesium hydroxide have settled. Then filter if necessary, remove 50 ml. of the clear liquid by a pipette and titrate this with decinormal sulphuric acid, using methyl orange as indicator. From the number of millilitres of acid used, the amount of alkali required to precipitate the salts may be found, and from this the permanent hardness is calculated (see example).

*Note.* During this reaction, the bicarbonates of calcium and magnesium will have been converted partially into carbonates, and precipitated :



Since, however, an equivalent of sodium bicarbonate is formed at the same time and remains in solution, no alkali will have been consumed in the process.

The **Total Hardness** may be obtained by adding together the temporary and the permanent hardnesses.

The hardness of water can also be measured by the electrometric method (p. 213). The chemistry of the process is exactly the same as above, but the end-points are shown by breaks in the potentiometric titration curves. In effect, the potentiometer is the indicator.

**Example.** The temporary hardness of a water, 500 ml. of the water required 8.4 ml. of decinormal sulphuric acid. Now 1 ml. of this acid corresponds with 0.005 gm. of  $\text{CaCO}_3$ ; therefore the weight of  $\text{CaCO}_3$ , which would neutralise the acid used in the titration, is

$$8.4 \times 0.005 = 0.042 \text{ gm.}$$

Hence the temporary hardness, as parts of calcium carbonate per 100,000,

$$= 200 \times 0.042 = 8.4.$$

In determining the permanent hardness, 250 ml. of the water were boiled with 50 ml. of a mixture of equal volumes of decinormal sodium hydroxide and decinormal sodium carbonate solutions, and, after filtration, the liquid was made up to 250 ml. Fifty millilitres of this liquid required 8.6 ml. of decinormal sulphuric acid for neutralisation. Hence the permanent hardness in the 50 ml. used corresponds with

$$10 - 8.6 = 1.4 \text{ ml. of decinormal acid,}$$

since 10 ml. of standard alkali were present in every 50 ml. of the solution. Therefore the number of millilitres of acid corresponding with the permanent hardness in the 250 ml. of the water used were

$$1.4 \times 5 = 7.0.$$

Now, since 1 ml. of the decinormal acid corresponds with 0.005 gm. of  $\text{CaCO}_3$ , the permanent hardness in 100,000 parts

$$= 7 \times 0.005 \times 400 = 14.0.$$

Hence the total hardness

$$= 14.0 + 8.4 = 22.4.$$

### Detection and Determination of Poisonous Metals in Water

Copper and lead are the most common poisonous metals in water; arsenic, barium, and zinc may be present in exceptional cases.

Copper and lead may be detected by placing 100 ml. of the water in a

Nessler cylinder and adding 10 ml. of normal acetic acid, and 10 ml. of a filtered saturated solution of hydrogen sulphide. If either metal is present in an appreciable amount, the tint of the well-mixed liquids will be darker than that of the same volume of water to which 10 ml. of acetic acid only have been added. Traces of these metals may be detected by evaporating a measured volume of the water to a small bulk before making the above test. If an appreciable colour is produced, the metals are determined colorimetrically.

**Copper.** Copper may be determined colorimetrically as copper ferrocyanide, or by the diethyldithiocarbamate method (p. 238).

If iron is also present it should be removed by adding a few drops of nitric acid, evaporating, and precipitating with an excess of ammonium hydroxide. The precipitate should be filtered off and dissolved in nitric acid, then precipitated once more by ammonium hydroxide, and again filtered off and washed. The precipitate may be used for the determination of iron (p. 368), and the combined filtrates for determination of copper.

**Lead.** If copper is absent, lead may be determined colorimetrically as lead sulphide (p. 242); if it is present, use the dithizone separation (p. 243).

*Action of Water on Lead.* Rain water, many natural soft waters, and waters containing natural vegetable acids act upon lead or its alloys if they remain in contact with it during storage or conveyance. It is therefore advisable to find out whether water intended for drinking purposes has any action upon lead. Hard waters do not as a rule act on lead unless they contain much carbonic acid. This is due to the fact that the hardening constituents rapidly form an insoluble, protective coating on the surface of the lead.

The behaviour of a sample of water towards lead may be tested as follows: Cut off two strips of lead sheet; scrape one of these so as to expose the bright surface of the metal, and leave the other in its tarnished condition. Immerse the lead strips in separate beakers of the water, and allow them to stand undisturbed for twenty-four hours. Then note the appearance of the lead and of the water.

If the surface of the lead has remained unchanged in appearance, and the water is perfectly clear and bright even after it has been shaken, the water has probably not acted upon the lead, since a white insoluble basic lead carbonate is usually formed by the action. To make sure whether any solvent action has occurred, however, it is best to remove the lead strips, and to test the water colorimetrically.

*The Relative Action of Samples of Different Waters* on lead may be assessed as follows:

A strip of sheet lead, 1.5 cm. wide, is scraped bright and is cut into lengths of 2.5 cm. Ten millilitres of each of the different water-samples are introduced into stoppered test-tubes, 15 cm. long and 2 cm. in diameter, and a strip of lead is completely immersed in each sample. The lead strips should be free from grease; they must therefore be handled by forceps, not by the fingers. The tubes are shaken to detach any air-bubbles from the lead, and are allowed to stand for one, three, seven or fourteen days, as required.

The water is poured off from each tube into a glass cylinder graduated

at 100 ml. capacity. The lead is rinsed in the tube by shaking it with about 10 ml. of distilled water, and this water is poured into the cylinder; the lead is removed and is rinsed by the jet of water from a wash-bottle to remove any adherent lead compound into the cylinder. Five millilitres of decinormal acetic acid are poured into the test-tube from which the lead strip has been removed, in order to dissolve any lead compound adhering to the glass: this acid is poured into the cylinder and the test-tube itself is finally rinsed out into the cylinder. The liquid in the cylinder is stirred until all lead compounds are dissolved and the liquid is quite clear: it is made up to the 100-ml. mark with water and the lead is determined colorimetrically by the sulphide process.

**Zinc** may conveniently be determined by the nephelometric method described on p. 250. Prepare a standard zinc solution, 1 ml. of which corresponds with 0.1 milligram of zinc, by dissolving 0.44 grm. of crystalline zinc sulphate in 1 litre of water. Add 2 ml. of 3 N.  $\text{H}_2\text{SO}_4$  and 1 ml. of 0.5 N.  $\text{K}_4\text{Fe}(\text{CN})_6$  to 50 ml. of the water-sample and match the turbidity caused by the precipitation of the zinc ferrocyanide with a sample similarly prepared by mixing 50 ml. of distilled water with a known quantity of the standard zinc solution and with the above quantities of  $\text{H}_2\text{SO}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  solutions. It is not advisable to add the zinc solution *after* the ferrocyanide or to use more than 1.5 ml. of the zinc solution. The tubes must be allowed to stand in the dark for five minutes before an attempt is made to match the turbidities.

When much iron is present in the water, it must be precipitated by adding  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ , boiling and filtering before determining the zinc.

### Determination of Major Mineral Constituents

**Silica.** Acidify 1 litre of the water with hydrochloric acid, and evaporate it to dryness. Dry the residue on a water-bath, and finally at  $110^\circ\text{C}$ . in an air-oven; then moisten it with hydrochloric acid, add water, and heat (see p. 100). Filter off any insoluble residue of silica, and wash, ignite it in a platinum crucible, and weigh. Treat the residue with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$ , and from the loss of weight calculate the amount of silica present. Keep the filtrate, and the residue in the crucible.

**Iron.** If the quantity present is small, it may be most readily determined colorimetrically by the thiocyanate method (p. 238). If it is large, proceed as follows:

**Iron and Calcium.** Add a few drops of concentrated nitric acid, free from iron, to the filtrate from the silica, and boil. Then add a little ammonium chloride solution, and a slight excess of ammonium hydroxide. Filter off and ignite the ferric hydroxide in the platinum crucible, together with the solid residue from the determination of the silica, and weigh the iron as  $\text{Fe}_2\text{O}_3$  (p. 64). This precipitate may contain a small quantity of

$\text{Al}_2\text{O}_3$  (p. 64). If it is desired to determine the latter, the iron in the mixed oxides is determined colorimetrically or volumetrically and the  $\text{Al}_2\text{O}_3$  is obtained by difference (p. 270).

Add excess of ammonium oxalate solution to the filtrate, allow the liquid to stand, filter off and ignite the calcium oxalate, and weigh as  $\text{CaO}$  (p. 70). A second precipitation of the iron and calcium is recommended if they are present in large quantities.

**Magnesium.** Evaporate the filtrate from the calcium precipitate to dryness, expel the ammonium salts from the residue by ignition, dissolve the residue in hydrochloric acid, add water, and filter if necessary. Then add a moderate excess of ammonium hydroxide, followed by an excess of sodium phosphate solution. Filter, wash and ignite the precipitate, and weigh the magnesium as pyrophosphate (p. 70).

**Sulphate.** Acidify 500 ml. of the water with hydrochloric acid and evaporate to about 100 ml. Add barium chloride solution in excess. Filter off, ignite, and weigh the precipitate of barium sulphate (p. 65).

**Alkali Metals.** Evaporate 1 litre of the water to about 100 ml. Precipitate the sulphate completely from this liquid by adding barium chloride solution. Filter, and boil the filtrate with milk of lime to precipitate the iron and magnesium. Filter, and precipitate the barium and calcium from the filtrate by adding ammonium hydroxide in excess, ammonium carbonate and a few drops of ammonium oxalate solution. Filter, evaporate the filtrate to dryness, and expel the ammonium salts from the residue by ignition.

Extract the residue with water, filter if necessary, and add 1 drop of ammonium oxalate solution in order to ensure that all the calcium has been precipitated. Filter again if necessary, acidify with hydrochloric acid, and evaporate to dryness in a weighed dish. Ignite the residue of alkali chlorides gently, and weigh it. The potassium chloride and sodium chloride in this residue may be determined separately if necessary (pp. 79-82).

### Dissolved Oxygen and Oxygen Demand

The amount of dissolved oxygen which a water contains originally, and especially the amount which it loses when kept, is a most important criterion of what may be termed "active organic pollution." An average potable fresh-water supply should contain from 6 to 7 ml. of oxygen per litre, and this amount should not diminish greatly when the water is stored.

**Winkler's Method** consists in absorbing the oxygen in a measured volume of the water by adding to the water a little manganous chloride solution followed by a solution containing potassium hydroxide and potassium iodide. The reaction is carried out in a stoppered bottle, which is completely filled with the liquids so as to avoid contact with air. The oxygen dissolved in the water converts a part of the precipitated manganous hydroxide into the higher hydroxide. Hydrochloric acid is added in excess, and the acid mixture is allowed to stand. After a time it is transferred to an open dish, and the iodine liberated by the higher

at 100 ml. capacity. The lead is rinsed in the tube by shaking it with about 10 ml. of distilled water, and this water is poured into the cylinder; the lead is removed and is rinsed by the jet of water from a wash-bottle to remove any adherent lead compound into the cylinder. Five millilitres of decinormal acetic acid are poured into the test-tube from which the lead strip has been removed, in order to dissolve any lead compound adhering to the glass: this acid is poured into the cylinder and the test-tube itself is finally rinsed out into the cylinder. The liquid in the cylinder is stirred until all lead compounds are dissolved and the liquid is quite clear: it is made up to the 100-ml. mark with water and the lead is determined colorimetrically by the sulphide process.

**Zinc** may conveniently be determined by the nephelometric method described on p. 250. Prepare a standard zinc solution, 1 ml. of which corresponds with 0.1 milligram of zinc, by dissolving 0.44 gm. of crystalline zinc sulphate in 1 litre of water. Add 2 ml. of 3 N.  $\text{H}_2\text{SO}_4$  and 1 ml. of 0.5 N.  $\text{K}_4\text{Fe}(\text{CN})_6$  to 50 ml. of the water-sample and match the turbidity caused by the precipitation of the zinc ferrocyanide with a sample similarly prepared by mixing 50 ml. of distilled water with a known quantity of the standard zinc solution and with the above quantities of  $\text{H}_2\text{SO}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  solutions. It is not advisable to add the zinc solution after the ferrocyanide or to use more than 1.5 ml. of the zinc solution. The tubes must be allowed to stand in the dark for five minutes before an attempt is made to match the turbidities.

When much iron is present in the water, it must be precipitated by adding  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ , boiling and filtering before determining the zinc.

### Determination of Major Mineral Constituents

**Silica.** Acidify 1 litre of the water with hydrochloric acid, and evaporate it to dryness. Dry the residue on a water-bath, and finally at  $110^\circ\text{C}$ . in an air-oven; then moisten it with hydrochloric acid, add water, and heat (see p. 100). Filter off any insoluble residue of silica, and wash, ignite it in a platinum crucible, and weigh. Treat the residue with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$ , and from the loss of weight calculate the amount of silica present. Keep the filtrate, and the residue in the crucible.

**Iron.** If the quantity present is small, it may be most readily determined colorimetrically by the thiocyanate method (p. 238). If it is large, proceed as follows:

**Iron and Calcium.** Add a few drops of concentrated nitric acid, free from iron, to the filtrate from the silica, and boil. Then add a little ammonium chloride solution, and a slight excess of ammonium hydroxide. Filter off and ignite the ferric hydroxide in the platinum crucible, together with the solid residue from the determination of the silica, and weigh the iron as  $\text{Fe}_2\text{O}_3$  (p. 64). This precipitate may contain a small quantity of

$\text{Al}_2\text{O}_3$  (p. 64). If it is desired to determine the latter, the iron in the mixed oxides is determined colorimetrically or volumetrically and the  $\text{Al}_2\text{O}_3$  is obtained by difference (p. 270).

Add excess of ammonium oxalate solution to the filtrate, allow the liquid to stand, filter off and ignite the calcium oxalate, and weigh as  $\text{CaO}$  (p. 70). A second precipitation of the iron and calcium is recommended if they are present in large quantities.

**Magnesium.** Evaporate the filtrate from the calcium precipitate to dryness, expel the ammonium salts from the residue by ignition, dissolve the residue in hydrochloric acid, add water, and filter if necessary. Then add a moderate excess of ammonium hydroxide, followed by an excess of sodium phosphate solution. Filter, wash and ignite the precipitate, and weigh the magnesium as pyrophosphate (p. 76).

**Sulphate.** Acidify 500 ml. of the water with hydrochloric acid and evaporate to about 100 ml. Add barium chloride solution in excess. Filter off, ignite, and weigh the precipitate of barium sulphate (p. 65).

**Alkali Metals.** Evaporate 1 litre of the water to about 100 ml. Precipitate the sulphate completely from this liquid by adding barium chloride solution. Filter, and boil the filtrate with milk of lime to precipitate the iron and magnesium. Filter, and precipitate the barium and calcium from the filtrate by adding ammonium hydroxide in excess, ammonium carbonate and a few drops of ammonium oxalate solution. Filter, evaporate the filtrate to dryness, and expel the ammonium salts from the residue by ignition.

Extract the residue with water, filter if necessary, and add 1 drop of chlorides gently, and weigh it. The potassium chloride and sodium chloride in this residue may be determined separately if necessary (pp. 79-82).

### Dissolved Oxygen and Oxygen Demand

The amount of dissolved oxygen which a water contains originally, and especially the amount which it loses when kept, is a most important criterion of what may be termed "active organic pollution." An average potable fresh-water supply should contain from 6 to 7 ml. of oxygen per litre, and this amount should not diminish greatly when the water is stored.

**Winkler's Method** consists in absorbing the oxygen in a measured volume of the water by adding to the water a little manganous chloride solution followed by a solution containing potassium hydroxide and potassium iodide. The reaction is carried out in a stoppered bottle, which is completely filled with the liquids so as to avoid contact with air. The oxygen dissolved in the water converts a part of the precipitated manganous hydroxide into the higher hydroxide. Hydrochloric acid is added in excess, and the acid mixture is allowed to stand. After a time it is transferred to an open dish, and the iodine liberated by the higher



manganese hydroxide is titrated with standard thiosulphate solution. From the amount of iodine thus found the percentage of dissolved oxygen can be calculated.

The process is comparable in regard to accuracy with gasometric methods and is much more readily carried out. The presence of nitrite in appreciable quantity affects the accuracy of the determination, and the nitrite must be oxidised to nitrate as described below before the analysis proper is commenced.

The Following Solutions will be required :

- (a) Concentrated sulphuric acid.
- (b) 0.125 N. potassium permanganate solution (3.94 grm. per litre).
- (c) Potassium oxalate solution containing 20 grm. of  $K_2C_2O_4 \cdot H_2O$  per litre.
- (d) Manganous chloride solution containing 33 grm. of  $MnCl_2 \cdot 4H_2O$  per 100 ml.
- (e) A solution containing 70 grm. of potassium hydroxide and 10 grm. of potassium iodide per 100 ml.
- (f) Concentrated hydrochloric acid, free from chlorine.
- (g) 0.05 N. sodium thiosulphate solution.

The manganese chloride must be free from iron ; and all the reagents must be free from nitrite, as is shown if the alkaline solution (e) does not yield an immediate blue colour if mixed with starch solution and acidified with the hydrochloric acid (f).

**Procedure.** Completely fill an accurately-stoppered, narrow-mouth bottle of from 300 to 400 ml. known capacity with the sample of water, carefully avoiding any unnecessary exposure of the water to the air. Then add 0.9 ml. of the sulphuric acid (a) and sufficient (1 to 2 ml.) of the permanganate solution (b) to leave the water slightly pink in colour. Mix the liquids by repeatedly inverting the stoppered bottle, and allow it to stand for ten minutes. The object of this procedure is to oxidise any nitrite present to nitrate. Then destroy any excess of permanganate by adding about 1 ml. of the oxalate solution (c). The bottle must in all these and subsequent operations be opened and re-stoppered as quickly as possible, and the reagents must be introduced to the bottom of the bottle by pipettes.

When the liquid has become decolorised, let exactly 1 ml. of the manganese chloride solution flow to the bottom of the bottle from a pipette, and add immediately 3 ml. of the mixed potassium hydroxide and iodide solution (e). Close the bottle, which must be full of liquid, without including any air bubble, and mix the liquids by inverting the vessel several times. The manganous hydroxide precipitate which forms will be more or less discoloured according to the amount of oxygen dissolved in the water.

Since the oxidation of the manganous hydroxide takes time and the action of light affects the result, the bottle is allowed to stand, shielded from light, for about fifteen minutes. When the precipitate has completely settled, remove approximately 100 ml. of the clear liquor with a pipette, without disturbing the precipitate, and add 5 ml. of the HCl (f). This will dissolve the precipitate, and the liquid will be coloured with free iodine

which can be titrated with the standard sodium thiosulphate (g) in the bottle. A correction should be made for the titration obtained in a blank experiment in which the sample is substituted by distilled water.

*The dissolved oxygen content is calculated as follows :*

If N = the number of millilitres of thiosulphate used,

S = the concentration of thiosulphate expressed as grammes of equivalent oxygen per millilitre. ( $O_2 = 4I = 4Na_2S_2O_3$ )

V = the volume of the bottle in millilitres.

The dissolved oxygen, in parts per 100,000 =  $\frac{100,000 \times N \times S}{V}$ .

The following is an example :

Volume of bottle = 321 ml.

$Na_2S_2O_3$  used = 6.95 ml.

Concentration of  $Na_2S_2O_3 = 0.000378$  gram. of oxygen per millilitre.

Hence dissolved oxygen per 100,000 parts of water

$$= \frac{0.000378 \times 6.95 \times 100,000}{321} = 0.8185.$$

Since 1,000 ml. of oxygen at  $0^\circ C.$  and 760 mm. weigh 1.44 gram., 100,000 ml. of the water contain

$$\frac{0.818 \times 1,000}{1.44} \text{ ml. of oxygen.}$$

Hence 1 litre of water contains 5.7 ml. of dissolved oxygen expressed at  $0^\circ C.$  and 760 mm.

**Oxygen Saturation.** The degree of aeration of a stream is measured in terms of the ratio of the dissolved oxygen (as found by the above method) to the

contain 1.47, 1.00 and 0.80 part per 100,000 of dissolved oxygen.

**Biological Oxygen Demand.** This determination is a valuable criterion of the capacity from a stream to determine

aerated water and again after five days at  $18.3^\circ C.$  The demand. The degree of dilution depends on the quality of the effluent; normally, 1 volume is diluted with 4 volumes of good tap-water, but with strong effluents 10 or even 50 volumes of water may be required. With unknown samples, therefore, it is advisable to make tests at several dilutions and to use the oxygen absorption (p. 354) as a guide.

**Procedure.** Make the necessary dilution and use the diluted mixture to fill two similar bottles of known volumes. Determine the dissolved oxygen in one of these as described above, and immerse the other in a thermostat at  $18.3^\circ C.$  for five days. Then make the same determination on this.

Calculate the dissolved oxygen in each case, as shown above, in parts per 100,000, and subtract the second from the first value. Multiply the resulting figure by the dilution used to obtain the biological oxygen demand.

**GENERAL REMARKS ON THE RESULTS OF THE CHEMICAL EXAMINATION OF WATER**

*Note.* The results of the above determinations are expressed in parts per 100,000; they can be converted into grains per gallon by multiplying by 0.7.

**Total Dissolved Solids.** Water which leaves a large residue on evaporation is not suitable for manufacturing purposes, because it produces scale in steam-boilers. It also leads to waste of soap in washing. Such water is not, however, necessarily undesirable for use as drinking water.

The amount of dissolved solids present in water depends mainly upon the nature of the soil through which the water has percolated. River water usually contains from 10 to 30 parts of dissolved matter per 100,000. Shallow well-water may contain from 25 to 200 parts or even more, the variation in this class of water being very great. Deep well-water may contain from 20 to 70 parts, but the proportion varies even beyond these limits in some cases.

The Ammonium Salts present in water are almost invariably of animal origin. Their presence usually points to recent sewage-contamination, since ammonia is one of the first products of change of nitrogenous animal refuse. The amount of ammonia which is present as ammonium salts in water varies greatly.

*Upland Surface-water and Shallow Well-water* contain on the average about 0.002 part per 100,000. If the land through which the water has passed is manured, the amount of ammonia it contains may rise to 0.03 or even higher. Generally, if the amount in drinking water exceeds 0.004 and albuminoid ammonia is also present, there is cause for suspicion.

*Deep Well-water* may contain as much as 0.1, but frequently contains no ammonia at all. The presence of a high proportion of ammonia in a deep well-water casts suspicion on the water if the albuminoid ammonia rises above a mere trace, or if any appreciable amount of oxygen is absorbed in the permanganate test.

*Spring-water* contains but little ammonia, seldom more than 0.01; the average amount is about 0.001.

*Sewage* may contain as much as 10 parts.

As a rule, it may be stated that the quality of the water must be considered suspicious if the water contains 0.006 part of ammonia per 100,000. If the amount of albuminoid ammonia present is more than a trace, even a smaller amount of free and saline ammonia should arouse suspicion.

**Albuminoid Ammonia**, as has been already explained (p. 354), gives an indication of the amount of organic nitrogenous matter present in the water. It should not exceed 0.008 part per 100,000, although in special cases, such as moorland water, a larger proportion may not condemn the supply.

**Oxygen Consumed by the Organic Matter.** The relative freedom from organic impurity may be judged from the results of the permanganate test. The oxygen absorbed by the organic matter should not exceed 0.05 part per 100,000 parts of water (0.10 part for upland surface waters).

Chloride is usually present in water as sodium chloride, occasionally as chloride of calcium or of some other metal. Sodium chloride may occasionally be derived from the soil. It may also be derived from sea-water, which has been either mixed with the water or introduced as spray, or is due to infiltration into wells near the coast. If no such source of the chloride can be traced, and its quantity exceeds 2 parts per 100,000, it may be derived from urine.

*Rain-water* usually contains sodium chloride, which has been derived from the air.

*Spring and River-water*, if they are unpolluted with animal refuse, usually contain less than 2 parts of chlorine as chloride per 100,000.

*Shallow Well-water* may contain almost any amount of chloride, the proportion depending on the extent to which sewage or surface-water has percolated into the well.

Nitrite, if it is present in any appreciable quantity, should be regarded as an indication of comparatively recent sewage contamination. Nitrite is readily oxidised to nitrate. Both nitrate and nitrite are innocuous, but they are usually oxidation-products of objectionable organic matter which was originally present in the water.

Nitrite in *Deep Well-water* has probably been produced by the reduction of nitrate. When nitrite is found in deep well-water, it is therefore not looked upon with as much suspicion as when it is found in *Shallow Well-water* or in *Upland Surface-water*, unless albuminoid ammonia or organic matter is also present in appreciable quantity.

**Nitrogen as Nitrite and Nitrate.** This value is of importance because when nitrogenous organic matter is fully oxidised, its nitrogen remains chiefly in the form of nitrate; but nitrite is also occasionally present if the oxidation is incomplete. Thus, the presence of a large amount of nitrogen as nitrite and nitrate points to past sewage contamination. This implies that, if the filtration and aeration which have caused the oxidation of the organic matter should fail, there will be the risk of recent unoxidised sewage-matter being present in the water. Such a risk is, however, practically absent in the case of water drawn from deep wells of good construction.

*Upland Surface-water*, if uncontaminated, should not contain more than 0.03 part of nitrogen as nitrate and nitrite per 100,000, although in cultivated districts the amount may reach 1 part per 100,000.

*In Shallow Well-water* the amount varies greatly.

*In Deep Well-water* the amount may rise to 5 parts, but the average is only 0.5.

**The Degree of Hardness** of water is chiefly of importance when the water is used for washing or for manufacturing purposes; or when it is used for generating steam in steam-boilers.

If water is required for drinking purposes, its hardness may vary from 2 to 50 parts per 100,000. Hardness within these limits seems to have no effect upon the health of the consumers, but a very hard water is not suitable for technical purposes. The character of the hardness will depend upon the nature of the soil with which the water has been in contact.

**Objectionable Metallic Constituents.** Opinions differ as to the allowable limits for certain metals in water, but probably those stated below will be generally accepted.

**Iron.** Not more than 0.1 part of iron per 100,000 should be present in water to be used for domestic and technical purposes: when as much as 0.3 part per 100,000 is present, the water has a distinct chalybeate taste. The amount is reducible by aeration or filtration.

**Copper** is very rarely found unless the water has been stored in copper vessels or has passed through copper pipes. Copper salts are also used to destroy algae and may be introduced into the water in that way. Not more than 0.1 part of copper per 100,000 of water is permissible.

**Zinc** has been found as a normal constituent of certain mineral waters; quantities varying from 0.0015 part of  $\text{ZnCO}_3$  and 13 parts of  $\text{ZnSO}_4$  per 100,000 have been found. It may also be introduced by contact of the water with galvanised iron pipes or tanks. Its presence in a drinking water is undesirable.

**Lead** has more often caused serious or fatal disturbances to health when taken in drinking water than any other metal. It is not a normal constituent of natural water, but is generally derived from contact of soft water with lead pipes or with lead-lined tanks. Its action will vary with different individuals, but generally speaking not more than 0.025 part per 100,000 of water may be present without producing an effect when the water is drunk: 0.05 is considered decidedly dangerous, while 0.095 part has proved fatal. Drinking water should undoubtedly be free from lead, as its physiological action is increased by the fact that lead accumulates in the system and is not continuously excreted.

**Dissolved Oxygen and Oxygen Demand.** A pure stream may have an oxygen saturation of 100 per cent. or more, especially in fine sunny weather, indicating supersaturation with oxygen; polluted streams however, may have values of 70 or less, although a figure between these two is not necessarily an indication of pollution, because in winter, when the weed life of the river is at low ebb, the evolution of oxygen from this source is less.

According to the findings of a Royal Commission which was concerned principally with sewage, an effluent is regarded as tending to be injurious if it has a biological oxygen demand exceeding 2 parts per 100,000 and contains more than 3 parts per 100,000 of suspended solids. Streams were classified as very clean, clean, fairly clean, of doubtful purity, and bad or polluted according as this value was not more than 0.1, 0.2, 0.3, 0.5 and 1.0 part per 100,000, respectively.

## SECTION XII

### ANALYSIS OF FOODSTUFFS

#### Analysis of Milk

The constituents of milk which are usually determined are the total solids, the ash and the fat. From them the amounts of water and of "solids not fat" are deduced. The casein and the milk-sugar, which are included in the latter, are rarely determined separately. The examination may frequently be hastened by determining the specific gravity of the milk and the percentage of total solids, and then calculating the percentage of fat present by the formula given on p. 379. If any doubt is thus raised as to the proportion of fat present, the fat may be determined directly by one of the four methods described.

The specific gravity of milk is determined by means of a Sprengel tube, specific gravity bottle or hydrometer. Although the Sprengel tube gives the most accurate results, it is customary to use a special form of hydrometer known as the Lactometer, particularly for dairy-control determinations. The scale readings of the Lactometer are marked in "degrees" over a range from 15 to 45, corresponding with specific gravities varying from 1.015 to 1.045.

**Total Solids.** Mix the sample of milk well by shaking it, and pipette 5 ml. into a tared platinum or porcelain dish. The dish should be shallow and of diameter 2 to 3 inches, so that the milk covers the bottom in a thin layer. Weigh the dish quickly in order to determine the weight of the milk. Add 1 ml. of acetone and evaporate the milk rapidly to dryness on a boiling water-bath. Transfer the dish with the residue to the steam-oven, and heat it for one hour. Cool, weigh; then repeat the heating for further periods of an hour each, until the difference between two consecutive weighings is not more than 1 milligram. Use this residue for the determination of the ash.

**Ash.** Ignite the residue in the platinum dish over a Bunsen or Argand flame, at a temperature which never greatly exceeds visible redness. If

may be hastened by crushing the carbonised residue from time to time with a platinum wire. The process is most easily carried out at a very dull red heat in a muffle furnace.

**The Werner-Schmidt Method for Fat.** The milk is mixed with hydrochloric acid and heated. The acid attacks the casein surrounding the fat-globules, and thus sets free the fat which rises to the surface. The fat is extracted by treating the mixture with successive quantities of ether; the ether solution is separated, the ether is distilled off, and the residue of fat is dried and weighed.

**Procedure.** Mix the milk well by shaking it, and determine its specific gravity. Measure accurately 10 ml. into the tube shown in Fig. 109. This tube is graduated at 20 ml. and at 50 ml. to facilitate the addition of the necessary volumes of acid and ether.

Add 10 ml. of concentrated hydrochloric acid, close the tube with a

cork and heat it in the water-bath for about ten minutes, shaking it occasionally. The liquid will become dark brown in colour, owing to the chemical action of the acid upon the casein, and the fat will collect on the surface. Now cool the liquid rapidly by holding the tube in a stream of cold water. When it is quite cold, fill the tube to the 50-ml. graduation with ether, which has been freed from alcohol by washing it repeatedly with water. Then insert the cork and shake the liquid vigorously for two minutes. When the ether has again risen to the surface, a small layer of undissolved matter will be seen between the ethereal and aqueous layers. Withdraw the ether solution into a weighed 100-ml. flask by means of a pipette. This is more conveniently done by inserting in the tube a fitting like that used in an ordinary wash-bottle, the curved end of the longer tube being adjusted so as to be just above the layer of suspended matter (see Fig. 109). The ethereal solution is easily transferred to the 100-ml. flask by blowing through the smaller tube.

Extract twice more, using two successive quantities of 20 ml. of ether, and add these extracts to that in the flask. Distil off the ether through a condenser, and heat the flask in the steam-oven for about twenty minutes. Cool it in a desiccator and weigh it.

The result gives the weight of fat in 10 ml. of milk.

**Example.** In an actual determination, 10 ml. (equal to 10.3 grm.) of milk were used. The ether extract yielded 0.347 grm. of fat.

Therefore the milk contained

$$\frac{100 \times 0.347}{10.3} = 3.37 \text{ per cent. of fat.}$$

**The Rose-Gottlieb Method for Fat.** Accurately measure or weigh 10 to 11 grm. of the milk into a narrow tube, 2 cm. in diameter and 100 ml. in capacity. The tube must be fitted with a rubber stopper. Add 1 ml. of ammonia solution of 0.880 sp. gr.

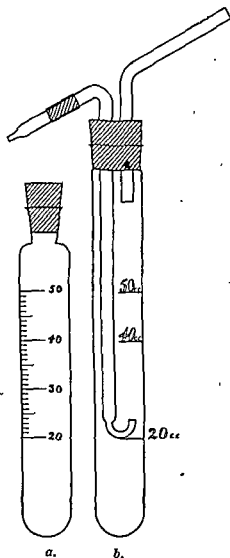


FIG. 109. SCHMIDT TUBE.

Mix the liquids gently, add 10 ml. of alcohol (about 95 per cent. by volume), and again mix gently, but without inverting the tube. Next add 25 ml. of methylated ether, of 0.720 sp. gr., and mix by inverting the tube four times. Then add 25 ml. of light petroleum, boiling below 60° C., and mix again by inverting the tube four times. The above directions for mixing the liquids after each addition must be carefully followed.

After the ethereal solution has separated, remove as much of it as possible by a pipette, or replace the stopper by the arrangement sketched in Fig. 109; and expel the ethereal solution, and collect it in a weighed flask. Mix the residual liquid with 25 ml. of a mixture of ether and light petroleum in equal volumes, avoiding any violent agitation, and remove as much as possible of the ether layer into the flask, repeating this treatment twice in a similar way with fresh quantities of the mixed ethers. Remove the ether by distillation and dry the flask in the steam-oven until its weight is constant.

If the milk is sour, lumps are sometimes seen after the ammonia has been added, but these will disappear if the tube is placed in warm water for a few minutes and is then well shaken.

**The Gerber Method for Fat.** This method requires the use of a centrifugal machine. The milk is treated with concentrated sulphuric acid which attacks the casein enclosing the fat globules. The fat, which is thus set free, is "separated" by whirling the milk round at high speed in a centrifuge. The Gerber method is rapid, and is consequently very widely used. Provided that standard apparatus and technique are employed, it produces results which are not only comparable among themselves, but which are in satisfactory agreement with those given by a gravimetric method such as the Röse-Gottlieb.

The tube used for this process is shown in Fig. 110. It consists of a fairly large reservoir, which can be closed by a tightly-fitting rubber stopper. The lower part of the reservoir is contracted and is graduated in "percentages of fat," the tube having been calibrated by working with milks of known fat content.

**Procedure.** Introduce 10 ml. of sulphuric acid, of density 1.820 to 1.825, into the tube, and then allow 11 ml. of the milk to trickle slowly down so that it does not mix with the acid. Add 1 ml. of amyl alcohol, of boiling-point 130° to 132° C. and density 0.814 to 0.816. Close the neck with a tightly-fitting rubber stopper, and, holding the stem in one hand and the stopper in the other, mix the contents by gently shaking the tube, finally inverting it several times so as to cause the acid to flow out of the stem and to mix with the rest of the liquid. Then place the tube, which will now have become very hot, in the centrifuge with the stopper outwards, and allow the machine to run for five minutes at a speed of from 1,000 to 2,000 revolutions per minute.

Stop the machine gradually, to prevent the risk of breaking the tube. Place the tube, with the stopper downwards, in a water-bath maintained

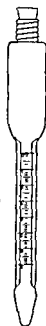


FIG. 110.  
GERBER  
TUBE.



at 60° to 65° C., and after five minutes read off the percentage of fat on the graduated stem. If the column of fat extends below the zero-mark, move the stopper gently inwards to bring the column completely on to the scale.

**Adams' Method for Fat.** A known weight of the well-mixed milk is absorbed by a strip of filter-paper. The filter-paper is dried, and the fat is extracted with ether in a Soxhlet apparatus.

By evaporating the milk to dryness on filter-paper, the residue obtained presents a very large surface to the solvent action of the ether, and the removal of the fat can therefore be completely effected. The extraction apparatus and the filter-paper, which are required for this process, are described below.

**The Soxhlet Extraction Apparatus.** The Soxhlet extractor consists of a reservoir (a), closed at the bottom, and sealed to a wide glass tube (b). Into the side of the reservoir near the top is fused a tube (c), which is joined to the tube (b), whilst into the reservoir at the bottom is inserted a narrower siphon-tube (d), which also makes connection with the tube (b), as indicated in Fig. 111.

The material to be extracted is placed in the reservoir (a) in such a way that the whole of it is below the top of the siphon-tube (d). It is usually wrapped in filter-paper, or, better still, is enclosed in an "extractor thimble," made of fat-free paper, of a size and shape suitable for use in the extractor. In this way, solid matter is prevented from passing into the reservoir and from thence being carried over with the solvent into the flask. The glass tube (b) of the extractor is attached to a flask (e), containing the solvent to be used, and a suitable condenser (f) is inserted into the upper end of the reservoir. Ordinary corks are generally used for this purpose, but they should first be extracted with the solvent to remove all soluble matter.

When the liquid in the flask (e) is boiled, its vapour passes up through the tube (b), and thence through the side-tube (c), since there is no direct communication between the reservoir and the tube (b). The vapour then passes into the condenser, and the condensed liquid drops back upon the substance in the reservoir, and accumulates in the reservoir.

As soon as the liquid reaches the level of the upper bend of the narrow siphon-tube (d), which communicates with the bottom of the reservoir, it siphons over and thus finds its way back again to the flask (e). This process will repeat itself as often as the liquid collects in the reservoir in sufficient quantity to reach the necessary level. In this way the substance is constantly brought into contact with the pure, warm solvent, and the matter thus extracted is carried by the solvent into the flask (e), where it will gradually accumulate.

**The Filter-paper Strip.** The strip is 58 cm. long and about 6 cm. wide.

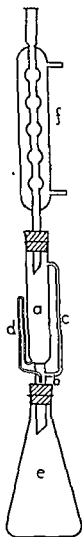


FIG. 111.  
THE SOXHLET  
EXTRACTOR.

Its exact width will be determined by the dimensions of the reservoir of the Soxhlet extraction apparatus (*a*, Fig. 111). The strip should be of such a width that when it is coiled up and placed in the reservoir of the Soxhlet apparatus it reaches nearly to the upper bend of the siphon-tube (*d*). Paper practically free from fat, and from other matter soluble in ether, may be obtained for this purpose. A strip of such paper, however, may contain from 4 to 5 mgrm. of matter soluble in ether, and this should either be extracted first or a correction made for it. If ordinary filter-paper is used it should be treated similarly.

*Extracting the Fat.* Pin the end of one of the paper strips to a cork held in the clamp of a retort stand, so that the strip hangs vertically. Then allow 5 ml. of the well-shaken milk to drop slowly upon the paper from a pipette and to be absorbed by it. Allow the strip to hang in a warm place until it is dry; and finally heat it for ten minutes in the steam-oven.

Then roll the paper into a coil, and place it in the Soxhlet extractor; an extraction thimble is not required. Pour about 100 ml. of dry ether into the weighed flask, and heat it on a water-bath sufficiently to keep the ether just boiling for three hours. If any suspended matter is present in the tared flask, the ethereal solution must be filtered through a tared paper into a second tared flask.

Remove the ether from the flask by distillation, add a few millilitres of absolute alcohol, and dry to constant weight in the steam-oven. The weight of the 5 ml. of milk taken can be obtained from its specific gravity, and hence the percentage by weight of the fat present in the milk can be calculated.

**The Other Principal Constituents of the Milk** are not determined directly, but their amounts are calculated from the results already obtained, as is described below:—

(a) **Water.** The percentage of total solids is subtracted from 100 to give the percentage of water.

(b) **"Solids not Fat."** The percentage of "solids not fat" is obtained by subtracting the percentage of fat from the percentage of total solids.

(c) **Determination of Fat by Calculation.** The results which have been obtained by the direct analysis of the milk may be checked by the following indirect method of calculation:

The specific gravity of milk is influenced by the amounts of fat and of "solids not fat" which are present, the former tending to lower the specific gravity, and the latter to raise it. Several formulæ, expressing the relationship of the quantity of fat to the specific gravity and the amount of total solids, have been proposed.

The following formula has been adapted by Richmond to the Adams' process of fat-extraction:

$$F = \frac{T}{1.2} - \frac{0.219 [(G \times 1000) - 1000]}{G},$$

in which *F* represents the percentage of fat, *T* the percentage of total solids, and *G* the specific gravity of the milk.

If a Richmond milk-scale is used, the percentage of fat can be read directly from the scale and the calculation is unnecessary.

operations. One-third of its total volume of glycerol is now added to the liquid, and it is again titrated with 0.1 N. NaOH solution until it becomes pink: Each millilitre of the decinormal alkali used in this last titration indicates the presence of 0.0062 grm. of  $H_3BO_3$ , or 0.0035 grm. of  $B_2O_3$ , or 0.0095 grm. of  $Na_2B_4O_7 \cdot 10H_2O$  in the volume of milk taken.

(b) *Formaldehyde* may be determined by a reagent consisting of a mixture of 1.6 ml. of normal nitric acid, with 100 ml. of concentrated hydrochloric acid.

Ten millilitres of the freshly-made reagent are added to 5 ml. of the milk in a test-tube, and the mixture, after being vigorously shaken, is kept for ten minutes in a water-bath at the temperature of  $50^\circ C.$ ; the liquid is then cooled rapidly to about  $15^\circ C.$  A violet coloration indicates the presence of formaldehyde in the milk. The amount of formaldehyde present may be determined by comparing the intensity of this coloration with that produced by each of several standard tubes containing milk to which known amounts of formaldehyde have been added, and which have been treated in precisely the same way. The reaction is most sensitive when from 0.2 to 6 parts of formaldehyde are present in a million parts of milk. If the colour is deeper than corresponds with 6 parts per million, the sample should be diluted with pure milk.

A rougher method consists in adding 1 ml. of dilute sulphuric acid, made by mixing the pure acid with three times its volume of water, to 100 grm. of the milk, and distilling the liquid. The amount of formaldehyde in 20 ml. of the distillate is then determined by the iodometric method (p. 169), and is multiplied by three, since the distillate will contain only about one-third of the formaldehyde which was originally present in the milk.

### Analysis of Butter

It is usual to determine the water, curd, salt and fat in butter. The addition of preservatives is illegal, but if a preservative such as boric acid is detected, it should be determined also. Again, if butter is to be tested for the addition of foreign fats, the butter-fat must be separated and examined further (p. 384).

**Water.** Weigh out accurately from 2 to 3 grm. of the butter into a flat-bottomed, tared dish; heat it for an hour on a water-bath or in a steam-oven, or in an air-oven at  $105^\circ C.$ , until no globules of water can be seen below the fat, and until the weight becomes constant.

**Curd and Salt.** Melt the dry butter in a dish and treat it with about 10 ml. of ether, pouring off the ether solution through a tared filter. Treat the residue again with ether, transfer it to the filter, and continue to wash it with ether until the last few drops of the ether give no residue when they are evaporated to dryness on a watch-glass. Then dry the filter and its contents to constant weight in a steam-oven. The weight of the residue represents the amount of curd, salt, and boric acid (if any). The dried filter is retained for the determination of the ash, and the ether solution for the direct determination of the fat.

It is possible, if care is taken, to pour off the ether solution from the curd without removing any of the latter, in which case, after all the fat

has been extracted, the dish itself may be dried in the oven and re-weighed. A tared filter-paper is thus rendered unnecessary. If the determination is carried out in this way, then both the curd and the salt may be determined separately. The residue in the dish is treated with hot water, which dissolves the salt, and is then transferred to a tared filter-paper. The filter-paper is washed with distilled water and dried to constant weight in the steam-oven. The result gives the amount of Curd present.

The water extract (and washings) contain the Salt, and this may be determined by titrating the extract with 0.1 N. silver nitrate, using potassium chromate as indicator (p. 193).

**Ash.** Transfer the dried filter containing the curd to a weighed platinum crucible, and ignite it at as low a temperature as possible, until the residue is white in colour and its weight is constant.

The residue should consist almost wholly of salt, but it may contain boric acid or borax introduced into the butter as a preservative. These may be detected by dissolving the ash in a little water and testing the solution by the method described on p. 381.

**Boric Acid.** Ten grammes of the butter are heated gently in a small evaporating-dish, and the melted fat is washed into a small, stoppered separating-funnel with about 30 ml. of boiling water. The whole is then shaken well and allowed to stand until the fat has separated completely from the water, when the water is allowed to flow off through the tap into a 100-ml. flask.

This treatment is repeated three times, not more than 20 ml. of boiling water being used on each occasion. The four washings are then cooled in the flask and diluted to 100 ml. with distilled water. Fifty millilitres of this filtered solution are acidified with HCl and boiled to expel  $\text{CO}_2$ . The solution is rendered just alkaline with 0.1 N. NaOH, using phenolphthalein as indicator. Two grammes of mannitol or 10 ml. of glycerol are then added. The solution is cooled and is titrated with 0.1 N. NaOH until a pink colour is seen. The percentage of boric acid present may then be calculated from this result, since 1 ml. of the 0.1 N. NaOH is equivalent to 0.0062 grm. of  $\text{H}_3\text{BO}_3$ .

Fat may be determined either by difference or directly; the latter is the more exact method.

If the fat is to be found by difference, the sum of the percentages of water, curd and salt, and boric acid or borax are subtracted from 100.

In the direct method, the ethereal solution and washings from the determination of the curd are transferred to a weighed flask, and the ether is removed by distillation. The flask containing the residue of fat is then heated for some time on a water-bath, and is finally dried in a steam-oven until its weight is constant.

**Acidity in Butter** is determined by the method described on p. 408, and may be returned in terms of butyric acid. Each millilitre of 0.1 N. alkali corresponds with 0.0088 grm. of butyric acid. *Rancidity* is usually accompanied by the formation of free fatty acids, and although rancidity cannot be correctly measured by the free acidity, the latter is useful in determining the quality and commercial value of the butter.

**Remarks on the Results of Butter Analysis.** The percentage of water present in well-made butter of good quality is not as a rule greater than 14.5, nor less than 11. A proportion exceeding 16 per cent., the legal limit, indicates either careless making or intentional adulteration.

The percentage of fat, which averages from 85 to 87, should never fall below 80.

### Detection of Foreign Fats in Butter

**Comparison of Butter-fat with other Edible Oils and Fats.** Butter-fat, like other natural fats (see p. 401), is a mixture of the triglycerides of fatty acids. The acids derived from butter-fat differ, however, from those derived from other natural oils and fats, in that they contain a considerable proportion of fatty acids which are volatile, soluble and of low molecular weight (see p. 508). Butyric acid, for example, forms from 3 to 4 per cent. of the total amount of fatty acids which can be separated from butter, and is a characteristic constituent of butter.

Cocoanut or palm-kernel oil yields a mixture of fatty acids of average molecular weight which are less soluble and less volatile than those derived from butter, so that adulteration of butter by such oils can be detected from the nature of the fatty acids.

The fatty acids in lard, and "oleo-margarine" butter-substitutes which contain beef-fat, are mainly insoluble, are of high molecular weight and are, therefore, for the most part, non-volatile.

The examination of butter for foreign fats is a matter of considerable difficulty. At one time, when the chief adulterants were lard and margarine, a low Reichert-Meissl value (Table, p. 389) was a fair indication of probable adulteration; but since cocoanut and palm-kernel oils have been used extensively for adulterating and cheapening butter, an adulteration as great as 20 per cent. may be present before this value becomes noticeably low. Additional tests have been devised by Polenske, who showed that cocoanut and palm-kernel oils furnished more *insoluble* volatile fatty acids than did butter (p. 387); and by Kirschner, who determined the amount of butyric acid in butter-fat by separating it as silver butyrate (p. 387).

The volatile fatty acids from different samples of butter are compared by separating the whole of the fatty acids from the butter and then distilling and collecting the volatile acids under standard conditions. The original method of effecting this was due to Reichert, but it has since been modified. The volatile fatty acids are subjected to further examination to obtain the Reichert-Meissl, Polenske and Kirschner values.

**Preparation of "Butter-fat," free from moisture, salt, and curd:** Melt some of the butter in a small beaker on a water-bath. When the fat is clear, pour it off through a dry filter-paper which is supported, without a funnel, in another small beaker on the water-bath. Care must be taken that none of the water from beneath the fat is poured on the filter, and the filtered liquid fat must be perfectly clear and transparent.

The *Reichert-Meissl Value* is defined as the soluble volatile fatty acids obtained from 5 grm. of fat, distilled under specified conditions, in terms of their equivalent in millilitres of 0.1 N. alkali.

The Reichert-Polenske Process for determining the volatile fatty acids in butter-fat is described below.

The apparatus employed is of standard size, and uniform conditions of manipulation must be adhered to strictly. Figs. 112 and 113 show the general arrangement of the apparatus, with dimensions in millimetres.

*Procedure.* Weigh 5 gramm. of the butter-fat into a 300-ml. flask, add 2 ml. of a 50 per cent. (by weight) solution of sodium hydroxide and

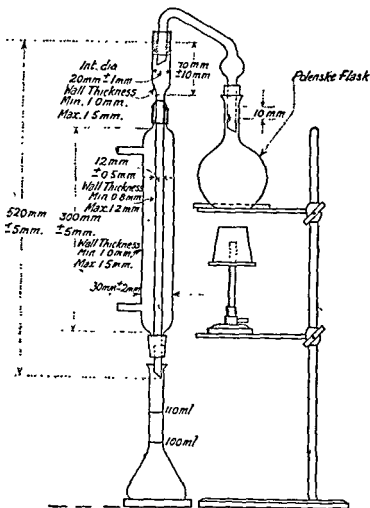


FIG. 112. STANDARD REICHERT-POLENSKE APPARATUS.

20 gramm. of glycerol. Heat the mixture with a small flame until frothing ceases and the solution becomes clear. Allow the liquid to cool somewhat, and then add very gradually 93 ml. of freshly-boiled distilled water. This is measured and added hot (at about 80° C. to 90° C.), and the liquid is shaken in order to prevent loss by frothing and to promote the solution of the soap.

Now add 50 ml. of sulphuric acid (of such concentration that 40 ml. neutralise 2 ml. of the sodium hydroxide solution used), drop in about 0.1 gramm. of powdered pumice, which has been sifted through butter muslin (or B.S. Sieve No. 50), quickly connect the flask with the

condenser, and heat it over a small flame until the layer of fatty acids has become quite clear. Then increase the size of the flame, and so regulate the distillation that 110 ml. of the distillate are obtained in about twenty-one minutes. When 110 ml. have distilled over, take away the flame, remove the receiving flask, and at once replace it by a 25-ml. cylinder which will receive any drippings.

Filter off the distillate from the receiving flask through a dry 9-cm. No. 4 Whatman filter-paper, rejecting the first runnings, and collect 100 ml. of it in a dry flask. Cork the flask and set it aside for the determination of the Reichert-Meissl value.

Wash the condenser tube with three successive 15-ml. portions of cold, distilled water and pass each washing separately and successively through the 25 ml. cylinder, the 110-ml. receiving-flask and the filter-paper. Reject the filtrate. Then rinse the condenser tube and the 25-ml. cylinder with three successive 15-ml. portions of neutral alcohol, pass each washing through the filter-paper and collect the filtrate in the 110-ml. flask. Cork the flask and set it aside for the determination of the Polenske value.

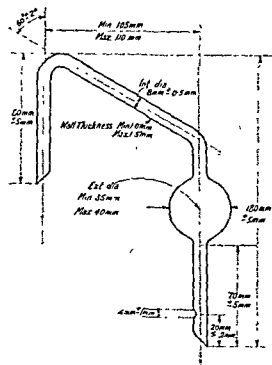


FIG. 113.

**The Reichert-Meissl Value.** Titrate the filtrate set aside for the purpose with decinormal sodium hydroxide or barium hydroxide, using 0.1 ml. of a 1 per cent. solution of phenolphthalein as the indicator. If the Kirschner value is to be found, use barium hydroxide.

The number of millilitres of decinormal alkali, less the number required for the blank experiment, when multiplied by 1.1, gives the Reichert-Meissl value.

It will be seen from the Table on p. 387, that the Reichert-Meissl value for pure butter-fat is high, 23 to 32, owing, as has been explained, to the presence of acids of low molecular weight, chiefly butyric acid. Although the Reichert-Meissl value varies widely, according to the food, country, period of lactation of the cow, and other causes, it very rarely falls below 24, and this number is officially recognised as the limit. It will be noticed that as cocoanut oil gives a value of 7 to 9 and palm-kernel oil a value of 5 to 6, the Reichert-Meissl value alone renders difficult the detection of even considerable percentages of these oils. It is therefore often necessary to determine the Polenske value also.

The determination of the Reichert-Meissl value, however, will serve to detect lard and most other animal fats, because the Reichert-Meissl values of these fats are below 1.

The insoluble fatty acids present in the 110-ml. flask are almost always opaque and white in the case of butter, while clear oily globules are present if cocoanut oil is present to the extent of over 10 per cent.

The Polenske Value is a measure of the volatile fatty acids, *insoluble* in water, obtainable from 5 grm. of fat, expressed in millilitres of decinormal alkali.

Titrate the alcohol filtrate, retained above, with decinormal sodium or barium hydroxide using 0.1 ml. of a 1 per cent. solution of phenolphthalein as the indicator. The number of millilitres used, less the number required for the blank, is termed the Polenske value.

The Polenske values in genuine butter are proportional to the Reichert-Meissl values, and vary from 1.6 for a butter with R.M. figure of 23, to 3.5 for one with R.M. figure of 32 (see Table below).

Comparison of the Reichert-Meissl Values with the Polenske Values of Butter-fat—

Reichert-Meissl Values .	32	31	30	29	28	27	26	25	24	23
Polenske Values .	3.5	3.2	3.0	2.9	2.8	2.4	2.0	1.8	1.7	1.6

The Polenske value is of use for determining the presence of cocoanut and palm-kernel oils in butter. These oils contain the glycerides of caproic, caprylic, capric and lauric acids, these acids being of average molecular weight, volatile in steam and partially or wholly insoluble in water.

Cocoanut oil gives a Polenske value of 15 to 18, and palm-kernel oil from 9 to 10, whereas butter-fat gives a much lower value, as is seen above. Polenske states that each increase in the value of 0.1 ml. on the figures shown in the Table corresponds with an addition of 1 per cent. of

of cocoanut or palm-kernel oil to the butter-fat.

The Kirschner Value is a measure of the soluble volatile fatty acids obtained from an oil or a fat having water-soluble silver salts. The number indicates what proportion of the volatile fatty acids is due to butyric acid, and therefore to butter-fat, since the volatile fatty acids from cocoanut and palm-kernel oils contain practically no butyric acid.

**Procedure.** To the solution, which has been neutralised by 0.1 N. baryta in the determination of the Reichert-Meissl value, add 0.5 grm. of powdered silver sulphate, insert the cork, and allow the flask to stand in the dark for one hour; shake occasionally. Filter and place 100 ml. of the filtrate in a 300-ml. Reichert-Polenske flask. Add 35 ml. of water, 10 ml. of the sulphuric acid previously used (p. 385) and a little pumice, and distil over 110 ml. in a precisely similar way to that described on p. 380. Filter, and titrate 100 ml. of the filtrate with 0.1 N. sodium hydroxide or baryta solution, using phenolphthalein as before. If the volume of decinormal alkali used, less that required for the blank determination is  $x$  ml.; and  $y$  ml. are required for 100 ml. of the Reichert-Meissl distillate:

$$\text{Kirschner value} = \frac{121(100 + y)}{10,000} \times x.$$



**Example,** The original Reichert-Meissl titration required 30.0 ml. 0.1 N. NaOH. The Kirschner titration required 15.0 ml. 0.1 N. NaOH; blank 0.5 ml.

$$\therefore \text{Kirschner value} = \frac{121 (100 + 30)}{10,000} \times 14.5 = 22.8.$$

The Kirschner numbers for pure butter-fat vary from 19 to 26 and are generally proportional to the Reichert-Meissl and Polenske values (see Table, p. 389). Coconut oil gives an average figure of 1.9 and palm-kernel oil of 1.0. Other fats and oils vary from 0.1 to 0.2.

Bolton and Revis give the following figures to show the relationship between the Kirschner value and the Polenske value :

Kirschner value (K)	.	.	.	20	22	24	26
Polenske value (P)	.	.	.	1.6	2.1	2.6	3.2

The formula  $P = (K - 14) \times 0.26$  gives results agreeing excellently with the mean figures. It may be safely assumed that if the Polenske figure is greater than  $(K - 10) \times 0.26$  the presence of coconut oil in butter-fat is established.

The Kirschner value offers little advantage over the Polenske value for the detection of coconut oil in butter, but shows if even a small proportion of butter-fat is present in a margarine containing coconut oil. This is because the Kirschner value for butter-fat is large compared with that for all other fats, owing to the presence of butyric acid in the butter-fat.

The following equation was suggested by Arnaud and Hawley for calculating the percentage of butter-fat in margarine: If  $K$  = Kirschner figure corrected for admixture,  $K'$  = Kirschner figure found,  $P$  = Polenske figure found, and 0.5 the Kirschner figure adopted for butter-free margarine; then :

$$K = (K' - 0.5) - \frac{P}{10}$$

$$\text{and, percentage of butter-fat} = \frac{100 K}{23}.$$

**General Remarks on the Detection of Foreign Fats and Oils in Butter.** A few qualitative tests (p. 417) should be carried out to ascertain whether any of the following oils are present. Thus, for *sesame oil*, Baudouin's test; for *cottonseed oil*, Halphen's test; *arachis oil*, Bellier's test.

In the quantitative examination of butter for foreign fats, considerable difficulty is experienced if coconut oil or palm-kernel oil is present; in their absence the determination of the foreign fats is simpler. Some mean values for some common edible oils are shown in the table on the following page.

It will be noticed that the values for butter differ greatly from those for the oils in the lower part of the Table. In the absence of coconut or palm-kernel oils, the percentage of foreign fats can be calculated from the minimum Reichert-Meissl number 24, as follows :

Let  $N$  represent the number of millilitres of decinormal alkali used for the neutralisation of the distillate from the butter-fat, and  $n$  the volume in millilitres of decinormal alkali required to neutralise the distillate in a

Table of Mean Values of some Edible Oils and Fats

(For fuller details, see p. 508)

	Specific gravity at 15° C.	Reichert-Meißl value.	Polenske value.	Kirschner value.	Saponification value.	Iodine value.	Insoluble fatty acids + unsaponifiable (Glycerol) value.
Butter-fat . . .	0.938	28	2.3	21	192.7	83	2.1
Cocoanut oil . . .	0.926	5.5	16.5	1.8	195.7	8.5	2.3
Palm-kernel oil . . .	0.932	5.5	9.8	1.07	194.6	14.5	2.3
Cottonseed oil . . .	0.923	below 1	below 1	—	193	110	2.5
Sesame oil . . .	0.920	below 1	below 1	—	192	105	2.5
Arachis oil . . .	0.9175	below 1	below 1	—	193	90	2.5
Lard . . .	0.936	0.6	below 1	—	196	62	2.5
Beef tallow . . .	0.947	0.5	below 1	—	195	43	2.5

*Note.* The analytical methods for some of the above values are fully described in the sections on Oils and Fats, p. 401 *et seq.*

blank determination in which no butter-fat has been used; then, since 5 grm. of normal butter-fat require 21 ml.,

$$1. \text{ The percentage of foreign fats} = \frac{21 - (N - n)}{21} \times 100.$$

This formula does not allow for the presence of volatile fatty acids in margarine; but if  $y$  represents the number of millilitres of decinormal alkali required to neutralise the volatile fatty acids in 5 grm. of margarine, then

$$2. \text{ The percentage of foreign fats} = \frac{21 - (N - n)}{21 - y} \times 100.$$

According to the Table,  $y$  varies from 0.5 to 1; the higher figure 1 may then be used for the calculation.

*Cocoanut and Palm-kernel Oils.* The insoluble volatile fatty acids in the receiver of the Reichert-Meißl apparatus should be examined; if they are liquid after being cooled to 15° C., cocoanut oil is probably present. The relation between the Reichert-Meißl figure and the Polenske value affords the best method of determining this oil. The Kirschner value, which is a measure of the butyric acid, is also of great assistance. When palm-kernel oil is present together with cocoanut oil, the determination of the separate proportions is very difficult.

Further information on this subject may be obtained from the references on p. 519.

*Calculation of the Percentage of Cocoanut Fat in a butter adulterated with cocoanut oil only, using the Reichert-Meißl value:* The Reichert-

Meissl value obtained experimentally was 21. Assuming the Reichert-Meissl value of pure butter-fat to be 28 and that of cocoanut oil to be 7:

If  $x$  = percentage of cocoanut fat,

$y$  = " " butter-fat,

Then  $x + y = 100$

and  $\frac{x}{100} \times 7 + \frac{y}{100} \times 28 = 21$

that is  $x + 4y = 300$

therefore  $3y = 200$

and  $y = 66.7$

Hence the percentage of cocoanut-oil fat = 33.3,

and " " " butter-fat = 66.7.

*Calculation of the Percentage of Cocoanut-oil Fat in a butter adulterated with cocoanut oil only, using the Reichert-Meissl and Polenske values:* The Polenske value obtained was 4.5, and the Reichert-Meissl number was 28. From the Table on p. 389 the corresponding Polenske ratio should be 2.7.

Now each excess of 0.1 ml. corresponds with an adulteration by 1 per cent.; therefore the percentage of cocoanut-oil fat =  $(4.5 - 2.7) \times 10 = 18$  per cent.

### Partial Analysis of Beer, Wine, and Spirits

It is usual to determine alcohol, acidity, and the total solid matter in solution in beer. The nitrogen present in the protein matter may be determined in the residue left on evaporation by means of the Kjeldahl process (p. 435). If the weight of nitrogen thus found is multiplied by 6.25, the approximate weight of albuminoids will be obtained.

For excise purposes it is necessary to determine the "original gravity" of the beer. This indicates the relative amount of solid matter which was in solution in the "wort" before it was fermented.

The examination of spirits is usually restricted to a determination of the alcohol content; this is relatively simple because spirits contain very little dissolved matter.

**Indirect Determination of the Alcohol in Spirits.** Determine accurately the specific gravity of the spirit at 15.5° C. (pp. 15-18), and then evaporate a measured volume to one-third of its original bulk to remove the alcohol. Cool and make up to the original volume with freshly-boiled distilled water. Mix this liquid well and then determine its specific gravity at 15.5° C. The specific gravity which the spirit would possess, if it were deprived of its dissolved matter, can then be calculated by adding 1 to the specific gravity of the spirit, and subtracting from this the specific gravity which has been found for the diluted residue. From the result the proportion of alcohol in the spirit can be found by reference to Alcohol Tables (pp. 500 and 501).

**Example.** The specific gravity of a sample of brandy was 0.95528; the residue which was left after evaporating a measured volume of the brandy to

one-third of its volume was made up to its original volume with distilled water, and then had a specific gravity of 1.00328. Hence the specific gravity of the brandy, if it were deprived of its dissolved solid matter, would be

$$1.95528 - 1.00328 = 0.95200.$$

From the alcohol Tables it is found that this specific gravity indicates the presence of 83.25 per cent. by weight of alcohol in the brandy.

**Determination of the Alcohol in Beer and Wine.** As beer and wine contain considerable amounts of dissolved matter, it is not possible to determine their alcohol content by the indirect method given above.

A volume of about 750 ml. of the liquid is freed from the greater part of the carbon dioxide which is dissolved in it. For this purpose the liquid is "tossed" by pouring it backwards and forwards from some height out of one vessel into another. The liquid is then distilled in an ordinary flask attached to an efficient condenser, or in the special apparatus which is shown in Fig. 114. This apparatus consists of a flask, about 1 litre in capacity, which is connected by means of a fairly wide glass tube with a vertical condenser consisting of a spiral inner tube of glass sealed into a broad glass jacket.

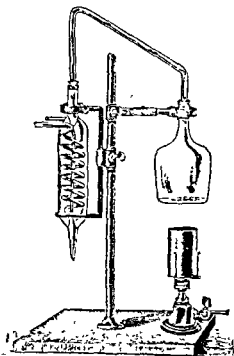


FIG. 114. REVENUE STILL FOR BEER OR WINE.

**Procedure.** Measure 250 ml. of the "tossed" liquid into the distillation-flask and connect the flask with the condenser and receiver; heat the flask with the flame of an Argand burner, until the liquid boils gently. When about two-thirds of the liquid have distilled over, transfer the distillate to a measuring-flask, make it up to the original volume of the liquid with distilled water, and mix it well. Then determine the specific gravity of this liquid at 15.5° C., either by direct weighing, or by means of a delicate hydrometer (p. 18).

The amount of proof-spirit or of absolute alcohol which is present in the liquid may be ascertained by reference to the Alcohol Tables (p. 500). In these Tables the specific gravity of water is taken as 1.

The residual liquid in the distillation-flask is allowed to cool; it is then diluted to the original volume of 250 ml., and its specific gravity is determined at 15.5 C. The number thus obtained is used in calculating the "original gravity" of the beer.

**Calculation of the "Original Gravity" of Beer.** The "original gravity" of a beer is the gravity of the wort from which the beer has been prepared. During the progress of fermentation, a part of the sugar present in the wort is converted into alcohol, with evolution of carbon dioxide. Conse-

quently the beer has a lower specific gravity than the wort from which it has been brewed. The specific gravity of the wort which would be required to produce a liquid of this specific gravity is determined by reference to the Table below, in which the degree of "spirit indication" is the difference between 1000 and the specific gravity of the alcoholic distillate, the specific gravity of water being taken as 1000.

The number thus obtained is added to the specific gravity of the liquid, which was produced by diluting the residue left in the distillation flask to 250 ml. The resulting number represents the original specific gravity of the wort.

Spirit Indication Table, showing Degrees of Gravity Lost

Degrees of Spirit Indication	0 0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.42	0.85	1.27	1.70	2.12	2.55	2.97	3.40	3.82
1	4.25	4.67	5.10	5.52	5.95	6.37	6.80	7.22	7.65	8.07
2	8.50	8.94	9.38	9.82	10.26	10.70	11.14	11.58	12.02	12.46
3	12.90	13.34	13.78	14.22	14.66	15.10	15.54	15.98	16.42	16.86
4	17.30	17.75	18.21	18.66	19.12	19.57	20.02	20.47	20.92	21.37
5	21.85	22.30	22.75	23.20	23.65	24.10	24.55	25.00	25.45	25.90
6	26.40	26.86	27.31	27.76	28.21	28.66	29.11	29.56	30.01	30.46
7	31.00	31.46	31.91	32.36	32.81	33.26	33.71	34.16	34.61	35.06
8										
9										
10										
11										
12										
13										
14										
15										
16	75.60	—	—	—	—	—	—	—	—	—

**Example.** If the specific gravity of water be taken as 1000, the gravity of the distillate will be less than 1000; suppose it to be 989.33. This number is deducted from 1000 and gives the "spirit indication," which in this case is 10.67. On referring to the table it will be seen that the corresponding number is 48.24, which represents the number of degrees of gravity lost in the production of the spirit during the fermentation of the wort.

If the specific gravity of the diluted residue from the distillation was 1023.42, the "original gravity" of the beer would be

$$1023.42 + 48.25 = 1071.66.$$

**Acidity of Beer.** Determine the acidity of 100 ml. of the "tossed" beer by means of 0.1 N.  $\text{NH}_4\text{OH}$  solution, using neutral litmus-paper as an indicator. This gives the total acidity. Then evaporate another portion of the beer to dryness on a water-bath; make it up to its original volume and determine the acidity, which is due in this case to the non-volatile acids present. The non-volatile acids are usually expressed as lactic acid, and the amount present can be calculated as a percentage by multiplying the number of millilitres of ammonium hydroxide used by 0.009. The difference between the number of millilitres of ammonium hydroxide used in the two determinations will give the amount of volatile acids; this is usually returned as acetic acid, and is calculated as a percentage by multiplying the number of millilitres by 0.006.

If the total acidity of beer expressed as acetic acid exceeds 0.1 per cent., allowance for it must be made in calculating the "original gravity" of the beer. For the method of applying this connection refer to Lloyd Hind's treatise on the subject (p. 519).

**Salt in Beer.** Sodium chloride is a normal constituent of beer and the average amount is about 50 grains per gallon; it is rarely added as an adulterant nowadays.

Evaporate 25 ml. of the beer to dryness in a platinum dish with 0.1 gm. of pure calcium hydroxide, and ignite the residue gently over an Argand burner until a grey ash remains. Triturate this residue in the dish with a little boiling water, and heat it on a water-bath for half an hour. Then transfer the whole with the washings to a 100-ml. flask, make up to 100 ml., shake well and allow the solid matter to settle. Transfer 50 ml. of the clear liquid to a flask, add a few drops of phenolphthalein solution and titrate with decinormal nitric acid until there is only a faint pink colour in the liquid. Add a few drops of potassium chromate solution and titrate the chloride with standard silver nitrate solution (p. 193).

The concentration of salt is expressed in grains per gallon; that is, in parts per 70,000.

### Analysis of Sugar

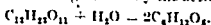
In the chemical examination of commercial sugars it is usual to determine moisture, ash, sucrose or cane sugar, and reducing sugars or glucose. Raw cane sugar, raw beet sugar or moist brown sugar may be used for practice in the methods of analysis described below.

**Moisture.** Weigh accurately 3 gm. of the sample in a weighed flat dish of nickel or other suitable material; heat in an air-oven at 105° C. for three hours, cool in a desiccator and weigh. From the loss of weight calculate the percentage of moisture.

**Ash.** Weigh out accurately 3 gm. of the sample in a tared platinum, silica or porcelain dish. Pour 1 ml. of concentrated sulphuric acid (free from non-volatile matter) over the sugar, add about an equal volume of water and heat carefully until the carbon rises as a porous sponge. Incinerate the mass at a dull red heat. In order to burn off the carbon completely, towards the end it may be necessary to stir with a stout platinum wire. It is usual to deduct one-tenth from the weight of the ash before calculating the percentage in the sample. If the weight of sugar taken was exactly 3 gm., the corrected percentage is obtained by multiplying the weight of the ash by 30.

**Sugar.** The sugar content of the sample may be determined either chemically or by means of the polarimeter as follows. The latter method is the faster and more accurate.

**Determination of Sucrose by Chemical Methods.** The main constituent of ordinary sugar is sucrose. This cannot be determined directly, but has to be first converted into "glucose" by the action of a dilute acid:



The process is known as "inversion," a name which is derived from the fact that whereas a solution of sucrose rotates the plane of polarisation of a beam of polarised light passing through it to the right, after the solution has been treated with acid the plane of polarisation is rotated to the left (see below).

*Note.* The product of "inversion" is actually a mixture of dextrose (glucose) and levulose in equal amounts, sometimes called "invert sugar." Dextrose and levulose each has the formula  $C_6H_{12}O_6$  and each reduces Fehling's solution. For convenience, the mixture is referred to below as "glucose."

The glucose formed by inversion is then determined volumetrically or gravimetrically by means of its reducing action upon Fehling's solution, an alkaline solution of copper. During the reaction the blue colour of the Fehling's solution disappears and red cuprous oxide is precipitated. In practice, the glucose originally present in the sugar is first determined; then, after inversion, the total amount of glucose is again determined. From the difference between the two, the amount of sucrose is obtained.

**Precautions.** It should be noted that solutions containing about 0.2 per cent. of glucose give the most consistent and accurate results in this method. If

yield constant results, or are comparable with one another, when they are carried out under precisely similar conditions; it is therefore necessary that the Fehling's solution should be standardised under exactly the same conditions as those under which the determinations are made. It must also be remembered that the reducing powers of the various sugars are different, even if the conditions remain the same. Thus, taking the copper-reducing value of invert sugar as 100, the amounts of the different sugars necessary to effect the same amount of reduction are respectively:

Invert sugar	100
Levulose	104
Dextrose	96
Maltose	161

The above numbers are based on the use of the weight of sugar and the conditions described below.

**Preparation of Fehling's Solution.** Solution No. 1 is prepared by dissolving 69.28 gm. of crystalline copper sulphate in water and diluting the solution to 1 litre.

Solution No. 2 is made by dissolving 346 gm. of crystalline Rochelle salt in hot water, mixing this with a solution containing 100 gm. of sodium hydroxide, cooling the mixture, and making it up to 1 litre.

Equal volumes of the two solutions, at room temperature, are measured into a dry flask, and are mixed by shaking. The mixture is Fehling's solution. The solutions may be stored separately, and the mixture should be prepared fresh daily.

The indicator formerly used was a solution containing ferrous ammonium sulphate and ammonium thiocyanate, but this must be used externally; it gives an uncertain end-point, and it is affected by iron salts. It is therefore now usually replaced by a 1 per cent. solution of methylene blue (Lane and Eynon's method) which, if used internally, is decolorised at the end-point.

**Standardisation of Fehling's Solution.** A solution of 0.95 grm. of pure sucrose in 150 ml. of water is boiled with 30 ml. of decinormal hydrochloric acid for one minute. The liquid is cooled, neutralised to phenolphthalein by the addition of 30 ml. of decinormal sodium hydroxide solution, and diluted with water to 500 ml. It will now contain 0.2 grm. of invert sugar in 100 ml.

**Preliminary Titration.** Treat 10 to 25 ml. of the Fehling's solution in a 300-ml. flask with 15 ml. of the sugar solution in the cold. Heat to boiling; after the liquid has boiled for fifteen seconds it will be possible to judge, from the bright red colour imparted to it, if nearly all the copper has been reduced. If it is judged that this is the case, add a few drops of indicator, and boil for two minutes. Then add the sugar solution 1 ml. at a time, boiling for ten seconds after each addition until the colour of the indicator has been completely discharged.

If after the treatment of the Fehling's solution with 15 ml. of the sugar solution there is much copper unreduced, a further 10 ml. of sugar solution, and so on, are added until it is considered unsafe to add a further large increment, when the rest of the titration is carried out as above. It is advisable not to add the indicator until the end-point has been nearly reached.

**Standard Method.** Ten or 25 ml. of Fehling's solution in a 300-ml. flask are treated in the cold with almost the whole of the sugar required to effect reduction (determined in the preliminary titration), so that if possible not more than 1 ml. of sugar solution is required in addition. The flask is heated over a wire gauze. After the liquid has reached boiling-point, it is kept boiling for two minutes, and then, without moving the flask, 3 to 5 drops of indicator are added; the titration is completed by the end of another minute, so that the liquid boils altogether for three minutes without interruption. The burette, which has an outlet tube bent twice at right angles, is held in the hand over the neck of the flask; a burette with a glass tap should not be used.

I and Eynon in  
the number of  
to 10 ml. of

Millilitres of sugar solution.	Invert sugar.	Invert sugar + 25 per cent of sucrose.	Dextrose	Levulose.	Maltose.	Lactose
15	50.5	43.4	49.1	52.5	77.2	64.9
20	50.9	43.2	49.5	52.5	76.8	64.6
25	51.2	42.8	49.8	52.8	76.4	64.5
30	51.5	42.5	50.1	53.2	76.0	64.4
35	51.8	42.2	50.4	53.4	75.7	64.5
40	52.0	41.8	50.6	53.6	75.4	64.5
45	52.3	41.4	50.9	53.9	75.2	64.7
50	52.5	41.0	51.1	54.0	75.1	64.9

The titration should be carried out rapidly, and the upper part of the flask should always be filled with steam to prevent contact of the liquid



with air, or the  $\text{Cu}_2\text{O}$  may redissolve. Near the end-point, the liquid is boiled for about ten seconds after each addition of the sugar solution. The first titration will usually only give an approximate result, and another will usually be necessary to establish the end-point with accuracy.

**Determination of the Sugar.** The glucose originally present in the sample is first found by titrating 10 ml. of Fehling's solution with a solution containing a known weight of the sugar, varying from 1 to 10 gm. in 100 ml. according to the amount of glucose present (see *Precautions*, p. 394).

An aqueous solution of the sugar sample is then prepared containing 10 gm. of sugar in 500 ml.; 50 ml. of this are inverted by being heated with hydrochloric acid as described under *Standardisation of Fehling's Solution*. The solution is neutralised, diluted to 500 ml., and is then titrated against 10 ml. of Fehling's solution.

The percentage of sucrose (S) is calculated by the formula,

$$S = \frac{95(I' - I)}{100},$$

where  $I'$  and  $I$  represent the percentages of glucose after and before inversion, respectively. From this the percentage by weight of sucrose can be calculated, because, since the relative weights of cane sugar and of the glucose obtained from it by inversion are as 342 : 360, it follows that, if the weight of the glucose found is multiplied by this ratio ( $= 0.95$ ), the weight of the sucrose from which the glucose has been derived will be obtained.

the percentage of glucose

$$= \frac{100 \times 100 \times 0.05}{5 \times 24} = 4.17.$$

The solution of the sugar was then inverted and neutralised, and then diluted until the solution represented 0.2 gm. of sugar per 100 ml. solution; 10 ml. of Fehling's solution required 27.5 ml. of this sugar solution. Therefore the total percentage of sugar, as glucose,

$$= \frac{100 \times 100 \times 0.05}{27.5 \times 0.2} = 90.91.$$

Hence the percentage of glucose equivalent to the cane sugar

$$= 90.91 - 4.17 = 86.74;$$

and the percentage of cane sugar

$$= 86.74 \times 0.95 = 82.4.$$

**Gravimetric Method.** Instead of titrating the sugar, its amount may be

and the weight of cuprous oxide which it can precipitate. This will involve making preliminary experiments with a known weight of pure cane sugar which has been inverted. The factors suggested for dextrose, levulose, and invert sugar are 0.5403 for  $\text{Cu}_2\text{O}$ , 0.4535 for  $\text{CuO}$ , and 0.5634 for  $\text{Cu}$ , and the weight of copper or of oxide of copper, when multiplied by the appropriate factor, should give the corresponding weight of sugar. These factors, however, vary

with the sugar and with differences in manipulation, and are, therefore, best determined in a preliminary experiment.

Brown, Morris and Millar give the reducing powers of 0.1 gm. of reducing sugars in terms of Cu and CuO as follows :—

Sugar.	Cu in gram.	CuO in gram.
Invert sugar . . . .	0 1941	0 2430
Levulose . . . . .	0 1862	0 2331
Dextrose . . . . .	0 2027	0 2538
Maltose . . . . .	0 1097	0 1373

filter papers (folded together to make a double filter), and washed twice by decantation with hot water, the precipitate being always kept under water to minimise oxidation. The filter is then washed well with hot water until the filtrate is no longer alkaline to litmus paper, and dried in the oven. The precipitate is then transferred to a piece of glazed white paper (as described on p. 51), the outer filter paper being used to wipe the glass funnel, and the papers are burned alone in a tared porcelain crucible. The precipitate is then added to the crucible and heating is continued for twenty minutes over a full flame, the crucible being tilted to allow free access of air. The crucible is allowed to cool in a desiccator for twenty

**Determination of Sugar by the Polarimeter.** This method is based on the fact that a beam of plane polarised light, on passing through a column of sugar solution, is rotated through a certain angle. This angle is dependent on the length of the column and on the nature and concentration of the solution.

The specific rotation of a sugar is the rotation obtained when a beam of polarised light is passed through a column of the solution, 1 decimetre in length, the concentration of the solution being 1 gm. per millilitre.

In practice, the rotation given by a solution of convenient concentration is observed and the specific rotation ( $\alpha$ ) is calculated from the formula :

$$[\alpha]_D = \frac{100 \times a}{l \times c}$$

where  $a$  is the observed angle of rotation of the yellow, D line of sodium light,

$l$  the length of the tube in decimetres, and

$c$  the number of grammes of the substance present in 100 ml. of the solution.

The specific rotation of sucrose, using sodium light ( $\text{D}$ ) for illumination, is  $+66.5^\circ$  at  $15^\circ \text{C}$ . It follows that the amount of sucrose can be determined by observing the angle of rotation in the polarimeter under proper conditions, provided that no other sugar is present.

It should be noted that the optical rotation of solutions of most sugars changes on standing, and only becomes constant after some time. Such solutions, however, attain their correct specific rotation immediately they are boiled.

**Saccharimeters.** These instruments are polarimeters which have been graduated in "sugar degrees," so that the percentage of cane sugar can be read off directly from the scale. The "normal weight" to use for a Soleil-Ventzke Saccharimeter is 26 gm.; this is the weight of the cane sugar which must be dissolved in water to give 100 ml. of solution at  $20^\circ \text{C}$ ., in order that the scale reading may give directly the percentage of cane sugar in the sample. Different forms of saccharimeter, however, have different "normal weights" of sugar.

The determination of cane sugar or sucrose in a sample which already contains glucose is carried out as follows:

A 10 per cent. solution of the sample is made and a direct reading of the rotation is obtained; the cane sugar is then inverted and the rotation given by the sample after inversion is observed. In the first reading the observed rotation is due to the cane sugar and the glucose originally present in the sample. By inversion the cane sugar is hydrolysed and converted into a mixture of equal quantities of dextrose and levulose, and therefore the rotatory power of the solution is changed.

The rotation due to sucrose is obtained by means of Clerget's formula, which is based on the rotation before and after inversion:

$$S = \frac{100(D - I)}{142.66 - 0.5t}$$

where  $S$  is the rotation due to the cane sugar originally present,

$D$  = the reading before inversion,

$I$  = the reading after inversion,

$t$  = temperature,  $^\circ \text{C}$ .

From this formula,  $S$  may be calculated, and the amount of cane sugar originally present in 100 ml. of the original solution may be found as follows:

Using the formula given on p. 397, we get,

$$66.5 = \frac{100 S}{l \times c} \text{ or } c = \frac{100 S}{66.5 \times l}$$

and since the observations are carried out on a  $t$ . solution, the percentage of sugar in the sample is

$$\frac{10 \times 100 \times S}{66.5 \times l}$$

**Example.** Ten gram  
rect reading of  
temperatu

$p$  were mad  
 $^\circ \text{C}$ ., and a  
tube.

; this  
ion

Then

$$S = \frac{100 [3.35 - (-3.0)]}{142.66 - 0.5 \times 12} = 4.70\%$$

and hence  $c = \frac{100 \times 4.79}{3 \times 66.5} = 3.60$  in a 10 per cent. solution of the syrup.

Hence the percentage of cane sugar in the syrup was 36.0.

The percentage of glucose present may be calculated as follows:

The amount of glucose in 100 ml. of solution, or in 10 gm. of the sugar syrup, as given by the formula, is :

$$\frac{100 [4.79 - 3.55]}{42.66 - 0.5 \times 12} = 338,$$

and the percentage of glucose will therefore be 33 %.

*Clarification.* In practice, commercial sugar solutions are sometimes so strongly coloured that it is difficult or impossible to obtain readings in the polarimeter until the solution has been subjected to a preliminary treatment. Such solutions are usually shaken well with a few grammes of animal charcoal and about 1 ml. of alumina-cream (Note) is added. The solution is made up to 100 ml., filtered through a dry paper, rejecting the first runnings, and examined in a 2-decimetre tube.

*Note.* Add the ammonium alum solution until a faintly acid reaction is obtained.

If the sugar solutions are very strongly coloured a more effective decolorising agent is required. Lead subacetate solution is suitable. This is made by heating together 30 gram. of lead acetate, 10 gram. of bismuth and 100 ml. of water, cooling and allowing the solution to settle. The clear liquid is used, in amount just sufficient to clarify and decolorise the sugar solution.

*Inversion of the Cane Sugar.* The inversion may be carried out as follows: Fifty millilitres of the filtered sugar solution are measured into a flask which is graduated at 55 ml. The solution is then made up to 55 ml. by the addition of concentrated hydrochloric acid. This acid liquid is now transferred to a conical flask, a thermometer is inserted into it, and the liquid is heated on a water-bath to 68° C. and is kept at that temperature for ten minutes.

The solution is cooled, made up again to 55 ml., and the polarimeter reading is taken in a 220-mm. tube. The use of the longer tube avoids the necessity for correcting for the dilution.

### Partial Analysis of Tea

The value of tea depends upon its inherent quality, and upon its freedom from adulteration. The following determinations enable a judgment to be formed on these points :

**Water.** Weigh out accurately about 3 gm. of the powdered tea into a pair of watch-glasses fitted with a clip, and heat it in a steam oven until the weight is constant.

**Ash.** Incinerate the dried tea, little by little, in a weighed platinum capsule or crucible at as low a temperature as possible, and weigh the residue. The total weight of ash thus obtained should not exceed 6 per cent.

## TEA ANALYSIS

Now add about 200 ml. of water to the ash and boil; then filter, and wash, dry, ignite and weigh the residue.

From these two determinations, the relation between the soluble and the insoluble matter in the ash may be calculated. This relation furnishes a valuable indication of the adulteration of tea with spent tea-leaves, since fresh tea-leaves contain a large proportion of soluble mineral matter which is dissolved out of the leaf during the "infusion". The ash of fresh tea-leaf always contains more than 50 per cent. of soluble matter.

**Tannin.** Extract about 10 gm. of the tea by boiling it repeatedly with fresh portions of water. Make up the clear extract to 1 litre, and determine the tannin present by the Löwenthal method (p. 337). This usually varies from 12 per cent. in black tea to 18 per cent. in green tea, but higher proportions occur in some teas.

Alternatively, boil 10 gm. of the powdered tea for half an hour under a reflux condenser with 800 ml. of water. Filter the solution while hot, and, when the filtrate has cooled, make it up to 1 litre. Shake 50 ml. of this extract three times with chloroform (30 ml. each time) to remove theine. Evaporate the aqueous solution to 20 ml., add 50 ml. of a saturated solution of cinchonine sulphate, and allow to stand for several hours. Filter through a Gooch crucible packed with asbestos, which has been washed with a half-saturated solution of cinchonine sulphate and dried at 100° C. Wash the precipitate with this same solution, dry *in vacuo* over sulphuric acid until most of the moisture has disappeared, and finally in an oven at 100° C., till the weight is constant. The dry precipitate contains 55 per cent. of its weight of tannin.

**Theine.** The value of tea depends largely upon the amount of theine which it contains. Determine this as follows: Extract 6 gm. of the tea with successive small portions of boiling water, allowing ten minutes for each "infusion," and mix the resulting extracts. Dilute the liquid with water to 600 ml., heat, add about 4 gm. of powdered lead acetate, and boil the liquid under a reflux condenser for ten minutes. Filter off 500 ml., corresponding with 5 gm. of the tea, through a dry filter, evaporate to about 50 ml., add 20 ml. of dilute sulphuric acid (1 in 6) and heat for thirty minutes (to destroy saponins). Cool, and filter into a separating-funnel. Extract with chloroform five times, using 25, 20, 20, 15 and 10 ml., respectively. Shake the combined chloroform extracts with 5 ml. of 1 per cent. NaOH solution and remove any theine which may have dissolved in the sodium hydroxide by extracting it with two successive portions of 10 ml. of chloroform. Combine the extracts in a weighed flask, remove the chloroform by distillation, dry at 100° C. and weigh the resulting theine.

The amount of theine present may vary from 1 to 3 per cent. according to the variety of the tea.

## SECTION XIII

### EXAMINATION OF OILS, FATS, WAXES AND SOAP

**Constitution of Fats and Oils.** The natural fats and oils are usually mixtures of the triglycerides of fatty acids of high molecular weight.

Thus olive oil consists mainly of glyceryl oleate or "triolein," and is represented by the formula  $C_3H_5(O.CO.C_{17}H_{33})_3$ . Similarly mutton fat contains the triglycerides of palmitic and stearic acids, which have the formulæ  $C_3H_5(O.CO.C_{15}H_{31})_3$  and  $C_3H_5(O.CO.C_{17}H_{35})_3$ , respectively, and are shortly named "tripalmitin" and "tristearin." The pure triglycerides are prepared with difficulty from the natural products, but they have been synthesised and their properties determined.

**Chemical Properties of the Natural Oils and Fats.** As has been already stated, most of the common fats and oils contain glycerides of palmitic, stearic and oleic acids, but there is considerable evidence that the acid radicals in combination with the three hydroxyl groups of the glycerol are not the same; the natural glycerides are thus said to be "mixed." Even when they have been purified, the oils usually contain colouring and gummy matter, alcohols, and other oil-soluble substances which are not saponifiable. These substances constitute the "unsaponifiable matter," the amount of which rarely exceeds 2 per cent. of the oil or fat. The most important of the unsaponifiable substances are the alcohols, cholesterol and phytosterol, which indicate the origin of the fat or oil.

When the oils and fats have been prepared by synthesis they are colourless, odourless, and tasteless; but the purest natural products frequently possess a characteristic colour, taste, or smell. Solutions of refined edible products should be practically neutral to indicators.

The natural glycerides either are liquid at atmospheric temperatures or their melting-points are low. All oils contain solid glycerides which separate out more or less completely on cooling; an oil is then said to be "demargarinated" (edible oil) or "racked" (cod liver oil).

The natural oils and fats are practically insoluble in water; are only slightly soluble in cold alcohol; and are somewhat more soluble in hot alcohol. They are, with one or two exceptions such as castor oil, freely soluble in most other organic liquids such as ether, light petroleum, carbon tetrachloride or chloroform. Their densities vary from 0.910 to 0.970. When they are heated to 260° C. little change occurs, except that polymerisation of drying oils takes place. At higher temperatures the fats decompose, and at and above 300° C. the characteristic penetrating odour of acrolein is apparent; at still higher temperatures fatty and aromatic hydrocarbons are given off in considerable amounts.

Exposure to dry air has no effect upon oils and fats, but ordinary damp atmospheric air in daylight exerts a marked influence on their composition. The change is most marked with drying oils such as linseed oil, oxygen being absorbed in large amount and the oil thickens and finally sets. The semi-drying oils absorb less oxygen, and the ordinary solid fats least of all. Exposure of the non-drying oils of low molecular weight (*e.g.*, butter

of the wax is then the same as that of the solution, which may be determined by means of a hydrometer (p. 18).

**Determination of the Melting-point.** The determination of the melting-point of fats and oils is not generally of much value, since melting often takes place so gradually that it is difficult to decide upon the exact temperature. Thus some operators select the point at which the fat begins to soften, and others the point at which the fat becomes perfectly transparent. The determinations must always be made under precisely similar conditions in order to be comparable.

For the determination of the melting-point of natural fats, the open-tube method (p. 18) may be employed. The fat is melted in order to insert it into the melting-point tube, but since a fat does not again attain its normal melting-point for some time after it has been melted, twenty-four hours at least must be allowed to elapse before its melting-point is determined (see also p. 18).

For technical purposes the point at which the top of the column of fat becomes clear and shows a meniscus is taken as the point of "incipient fusion," and the temperature at which the column becomes clear that of "complete fusion." The relation of these two temperatures is of value in judging the utility of a fat for certain purposes.

The melting-point of a wax is more definite than that of a fat, and is of value as a guide to purity.

**The "Titre" Test.** The actual solidifying-point of a fat or oil, as given by the temperature at which turbidity begins, is very difficult to observe. Advantage is therefore taken of the fact that, when a liquid is carefully cooled, the temperature will fall below the solidifying-point before solid separates out; then, if the liquid is vigorously stirred, solidification accompanied by a rise of temperature occurs. The highest temperature reached is the solidifying-point.

It has been found, however, that the mixed fatty acids derived from the fat or oil give much more definite results than the fat or oil itself, and these are accordingly used in the "Titre" test. The details of the method must be followed carefully if comparable results are to be obtained.

**The Apparatus required** (Fig. 115) is a test-tube, measuring 16 cm. by 3.5 cm., supplied with a loosely-fitting cork through which passes a thermometer reading to 0.1° C. The test-tube is inserted through a cork which closes the mouth of a large bottle, 10 cm. in diameter and 13 cm. high, so that it rests centrally with its end 3 cm. from the bottom of the bottle. The bottle serves as an air-jacket for the test-tube.

Sufficient of the mixed fatty acids (30 to 40 grm.) is prepared from the oil by the method given on p. 414. Great care must be taken to obtain

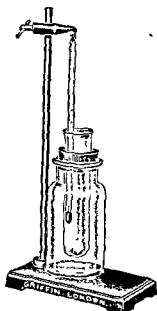


FIG. 115. TITRE TEST.

them as pure as possible, and quite free from moisture. The fatty acids are melted to a clear liquid by warming them on a water-bath, and enough of this liquid to cover the bulb of the thermometer completely, when the latter is in position, is poured into the test-tube. The liquid is allowed to cool. As soon as any turbidity is observed the liquid is stirred by means of the thermometer. This is carried out systematically by stirring three times in one direction, three times in the other and then continuously, taking care not to touch the sides of the test-tube with the thermometer. The temperature will rise sharply at first, remain steady and then begin to fall. The highest temperature reached is recorded as the solidifying-point. Duplicate determinations should not differ by more than  $0.1^{\circ}\text{C}$ .

The following are the "titres" (in  $^{\circ}\text{C}$ .) of some fatty acids:—

Cocoanut Oil	22 to 15	Olive Oil	17 to 26
Palm Kernel Oil	20 „ 25	Arachis Oil	28
Tallow (Beef)	38 „ 48	Cottonseed Oil	32 to 35
Tallow (Mutton)	40 „ 48	Maize Oil	19
Palm Oil	35 „ 45	Linseed Oil	18 to 20
Lard	42	Soya Oil	21

The "titre" test is a standard test in the evaluation of tallows. It is of use in choosing fats for soap manufacture, since, in general, the "harder" a soap, the higher the "titre" value of the fatty acids contained in it.

**Heat of Reaction with Sulphuric Acid (Maumené Test).** This is a simple and rapid test for a drying oil and is based on the fact that when concentrated sulphuric acid is mixed with a drying oil, a greater rise of temperature occurs than when it is mixed with a non-drying oil. Results of great accuracy cannot be obtained, but the test is useful where only an indication of the nature of the oil is required. Comparable results can be obtained only when the experiments with different oils are conducted under exactly similar conditions. It is essential that the acid should always be of the same concentration, which must be not less than 95 per cent., and that it should in every case be at the same initial temperature; the containing vessels should also be similar in shape and capacity.

Prepare a "nest" of cotton-wool for a 200-ml. beaker, by placing cotton-wool or wadding in a larger beaker. Then weigh accurately 50 gm. of the oil into the smaller beaker, and place this beaker and a bottle of concentrated sulphuric acid in cold water. As soon as the temperature of the oil and the acid are the same, take out the beaker of oil, dry it on the outside and place it in the nest of cotton-wool. Stir the oil with a thermometer, take its temperature accurately, and allow 10 ml. of the acid to flow in slowly from a pipette. The acid must take one minute to flow into the oil, and during this time the oil must be stirred continuously. The highest temperature reached during this process is recorded.

In order to eliminate the error due to the use of acids of different concentration, the rise in temperature may be compared with that obtained by treating 50 ml. of water with the acid in exactly the same manner as the oil was treated. The rise in temperature during an experiment with oil is termed the "temperature reaction," and this is referred to that obtained with water as 100; thus:



$$\frac{\text{Rise of temperature with oil} \times 100}{\text{Rise of temperature with water}} = \text{Specific temperature reaction.}$$

Among other physical characteristics of an oil or fat, the **Refractive Index** is one of the most useful for identification. For a description of the method of determination, see the references on p. 519. If it is desired to obtain this value for a very small quantity of sample (e.g., a few drops of oil) this may conveniently be done, without special apparatus, by placing a drop of the sample in a number of liquids, of known refractive index, in which it is insoluble; the refractive index of the liquid in which the oil is invisible then equals that of the oil. Lists of suitable liquids are to be found in *Hackh's Chemical Dictionary* (p. 520). Alternatively, crystals of known refractive index may be immersed in the drop of oil until one is found which is invisible.

**Water.** Weigh accurately about 5 gm. of the fat or oil in a tared dish, about 6 cm. in diameter and containing a thin glass rod, which must be weighed with the empty dish. Heat the whole in an air-oven at a temperature of from 100° to 110° C. until the weight is practically constant.

The drying should be stopped as soon as two successive weighings agree to within 1 or 2 mgrm. This will usually be the case after about two or three hours. If the heating is continued further, some of the lower fatty acids may be volatilised, or possibly an increase in weight may take place owing to absorption of oxygen from the air. While the fat is being dried, it should be stirred from time to time, because any water which collects below the melted fat will evaporate very slowly, unless it is brought to the surface.

With "drying oils," which absorb oxygen readily from the air, 10 gm. of the fat or oil should be placed in a small wide-mouthed flask and heated at 105° C. to 110° C. for thirty minutes in a current of dry CO<sub>2</sub>.

If the oil contains volatile substances, proceed as follows:—

100 ml. of the oil are measured out in a dry,

tube," the latter having 10 ml. of its lower portion graduated in 0.1 ml. (see Fig. 116). The tube is joined to a condenser and xylene is poured down this until the graduated portion of the distilling-tube is full.

The round-bottomed flask is heated in an oil-bath so that the contents distil. In doing so, the moisture is carried over and is condensed along with the xylene. The xylene overflows continuously back into the distilling-flask, but the drops of water collect in

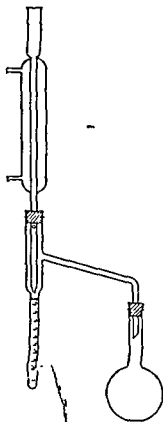


FIG. 116. DETERMINATION OF WATER IN OILS, FATS AND WAXES.

the bottom of the graduated tube and coalesce. After boiling for about an hour, all the moisture will have been removed, and the volume of water may be read off.

### Foreign Substances

Impurities, such as mineral matter and animal and vegetable tissues, are determined by weighing the residue after removing the fat with a solvent, e.g., light petroleum or ordinary ether.

Weigh out accurately into a flask 10 to 20 gm. of the dried fat, and shake this with light petroleum (B.P. 40° to 60° C.); pour the solution through a tared, ashless filter-paper, and wash the residue with fresh solvent until a few drops of the washing liquid, when evaporated on paper, do not leave a grease spot.

Dry the filter and its contents at 100° C. and weigh. The mineral matter is found by igniting the filter and its contents at a red heat and weighing the ash: the organic matter is found by difference.

*The Mineral Residue* may contain salt, chalk, clay, lime and alumina, the latter substances being derived from mineral soaps present in the fat.

*The Substances Soluble in Water* may be removed by shaking from 50 to 100 gm. of the original fat with hot water in a separating-funnel; the water layer, which separates out on standing, may be tested for acid or alkali, and these substances, if present, may be determined volumetrically. Evaporation of a portion of the aqueous layer will give the total amount of water-soluble substances, and the residue may be tested for metallic salts, soaps and starch by the usual methods.

*The Determinations of Fat and Foreign Substances* may be combined by using a Soxhlet extractor (p. 378) as is described below:

Weigh out accurately from 10 to 20 gm. of the fat into a "Soxhlet thimble," or into a cartridge made by rolling a strip of fat-free filter-paper round a wooden cylinder and folding it in at one end. Fold a small filter-paper into a cone, insert this into the mouth of the thimble and place the thimble in the extractor. The filter-paper will prevent any solid matter from escaping from the thimble during the extraction. If a cartridge of filter-paper is used, pinch the top of the paper together so as to enclose the fat.

Now pour 50 ml. of light petroleum (B.P. 40° to 60° C.) into the lower flask, which should have a capacity of about 150 ml., and pour the solvent also into the Soxhlet apparatus through the reflux condenser until it begins to siphon over; heat the flask on a water-bath. The amount of liquid which condenses should cause the siphon to empty the reservoir of the Soxhlet apparatus from 20 to 30 times in an hour.

The extraction of the fat, which will require about an hour, is known to be complete when a few drops of the solvent, taken as they come from the siphon, leave no grease spot when they are evaporated on filter-paper. As soon as this is the case, remove the thimble and distil the solvent from the flask of the extractor, emptying this each time that it fills. When

the bulk of the solvent has been distilled off, dry the residual fat at 100° C. to 110° C. in a current of dry CO<sub>2</sub> until its weight is approximately constant (p. 406). If the fat is of known origin and unlikely to be affected by exposure to the air, it may be dried directly in an oven.

**Detection and Determination of Inorganic Substances Dissolved in the Fatty Matter.** Oils and fats have the property of dissolving small quantities of metals and forming metallic soaps, and soaps of lead and manganese are often introduced into "boiled oils."

Ten grammes of the fat are carefully incinerated in a porcelain dish and the residue is examined qualitatively. If the amount of ash is appreciable, an approximate quantitative analysis may be carried out. Individual metals, *e.g.*, iron, copper, lead, manganese, can be determined colorimetrically (see pp. 234 *et seq.*).

## CHEMICAL EXAMINATION OF OILS, FATS AND WAXES

### The Acid Value

The Acid Value is defined as the Number of Milligrams of Potassium Hydroxide which are required to neutralise the Free Fatty Acids present in One Gramme of the Fat or Wax. Freshly-prepared animal oils and fats contain practically no free fatty acids, and vegetable oils from fresh seeds usually contain only small amounts, but the quantity of free acid increases on keeping, owing to hydrolysis and oxidation. The presence of free fatty acids in an oil or fat is always to be deprecated. It imparts a sharp and unpleasant flavour to edible oils; causes corrosion when present in lubricating oils; and is injurious in oils and fats used for pharmaceutical or medicinal purposes.

For the determination, about 10 grm. of the fat or oil (*Note 1*), according to its acidity, are weighed accurately into a flask, and 50 ml. of purified methylated spirit are added (*Note 2*). On the other hand, hard waxes should be warmed if necessary, and dissolved in 50 ml. of ether; 50 ml. of the methylated spirit are then added. These solvents should be neutral, or allowance must be made for a blank titration on them. One millilitre of a 1 per cent. phenolphthalein solution is added and 0.5 N. potassium hydroxide solution is added from a burette until a pink colour remains in the liquid for a few seconds after it has been well shaken; 0.1 N. alkali solution may be used if the acidity is low. Long-continued shaking causes the colour to disappear owing to neutralisation of the excess of potassium hydroxide by saponification.

The Calculation of the Acid Value is shown by the following example:

3.254 grm. of a particular sample of tallow required 3.5 ml. of decinormal potassium hydroxide solution: hence the free fatty acids present neutralised  $3.5 \times 5.61 = 19.64$  milligrams of KOH, and, since the acid value (A) is the weight of KOH in milligrams required to neutralise 1 grm. of tallow,

$$A = \frac{3.5 \times 5.61}{3.254} = 6.03.$$

If the nature of the fatty acid is known, its percentage may be calculated from the following data.

1 ml. of normal KOH = 0.256 grm. of Palmitic Acid.

" " " = 0.284 " Stearic "

" " " = 0.282 " Oleic "

In this country the percentage of free acid is usually returned as if it were all oleic acid, and the acid in the above sample would thus be returned as equivalent to

$$\frac{3.5 \times 0.0282}{3.254} \times 100 = 3.03 \text{ per cent. of oleic acid.}$$

With cocoanut, palm-kernel, balassu and cohune oils the factor 0.0200 is substituted for 0.0282, and the free acid is returned as "lauric acid."

*Note 1.* The presence of mineral acid may be detected by shaking the fat or oil with a little hot water, and noting whether the water is reddened by a drop of methyl orange solution. Mineral acid, if present, should be removed at once by washing the fat repeatedly with fresh portions of boiling water. It may be determined by titrating the washings, using methyl orange as indicator.

*Note 2.* The methylated spirit is purified by allowing it to stand over solid sodium hydroxide and then by distilling it. Before it is used, a few drops of phenolphthalein are added and then decinormal potassium hydroxide solution until a permanent faint pink colour is produced.

### The Saponification Value, or Koettstorfer Value

The Saponification or Koettstorfer Value is the Number of Milligrams of Potassium Hydroxide which are required for the Complete Saponification of One Gramme of an Oil, Fat or Wax. The following solutions are required :

(a) *Standard Hydrochloric Acid.* A seminormal solution.

(b) *Alcoholic Solution of Potassium Hydroxide.* Dissolve 28 grm. of potassium hydroxide, which has been "purified from alcohol," in a little water, and make up the volume of this solution to 1 litre either with alcohol of 0.81 specific gravity, or with purified methylated spirit. Allow the alcoholic solution to stand for twenty-four hours, and then filter it into a litre bottle. Protect the solution from the air. This bottle should be closed by a perforated rubber stopper in which is fitted a 25-ml. pipette. A piece of rubber tube closed by a piece of glass rod is slipped over the upper end of the pipette.

**Procedure.** Weigh accurately about 2 grm. of the purified and filtered fat into a 200-ml. flask. Then add 25 ml. of the alcoholic potash solution (b) by means of the pipette attached to the rubber stopper, allowing 3 drops to fall after the stream has stopped. Now attach a reflux condenser to the neck of the flask and heat it in the water-bath for about thirty minutes (at least one hour for a wax). The contents of the flask should just simmer and should be shaken from time to time.

As soon as saponification is complete and the solution is clear, add 1 ml. of a 1 per cent. solution of phenolphthalein and titrate the excess of alkali with the standard hydrochloric acid (a).

At the same time carry out a blank experiment, in which the same amount of alcoholic potash, delivered in the same way from the pipette, is heated in the same way as in the actual determination, and is finally titrated similarly. This is necessary in order to eliminate all sources of

disturbance, such as that due to the presence of carbon dioxide. The difference between the amounts of potash used in the two titrations is the quantity which is required to saponify the fat. The number of milligrams of potash which would be required for 1 gm. of the fat is calculated from this.

In an Actual Determination with Olive-oil, the following results were obtained. Twenty-five ml. of the KOH solution were added to 1.532 gm. of olive-oil. After saponification, 12 ml. of seminormal hydrochloric acid were required for neutralisation. In the blank test, 25 ml. of the alkali solution required 22.5 ml. of the acid for neutralisation. Hence the volume of potash solution required for the saponification is equivalent to

$$22.5 - 12.0 = 10.5 \text{ ml.}$$

of seminormal hydrochloric acid, and contains

$$\frac{10.5 \times 56.1}{2} = 294.5 \text{ milligrams of KOH ;}$$

and 1 gm. of the oil would therefore require

$$\frac{294.5}{1.532} = 192.4 \text{ milligrams}$$

of KOH for its saponification. This figure is the "saponification" value.

The Saponification Value varies with the nature of the fatty acid ; the lower the molecular weight of the fatty acid radical present, the greater will be the weight of potash required for the neutralisation of a given weight of the acid, and the higher the saponification value.

The saponification value does not vary greatly for the same substance, but it is affected by the presence of free fatty acids, which tend to increase it, and by slight differences in the composition of the fats, which may arise from differences in locality and soil and from other natural causes.

The Table on p. 508 shows the saponification values of the common oils, fats and waxes. It will be seen that waxes are characterised by low saponification values, and that therefore a ready means of distinguishing waxes from oils and fats is available.

It will also be noticed that the majority of oils and fats have a saponification value which approximates to 193. Deviations from this number are characteristic of certain oils ; thus while rape-oil and castor-oil have low saponification values, some of the fish-oils and butter possess relatively high values. Saponification values greater than 200 are characteristic of oils of the cocoanut and palm-kernel groups. Values above 200 usually point to the presence of one or more of these oils in a mixture.

### Unsaponifiable Matter

The term "Unsaponifiable Matter" is applied to Substances which are Insoluble in Water and which cannot be saponified by Caustic Alkali with the production of Soluble Soaps. Oils and fats usually contain only small quantities of unsaponifiable matter. The method described below is only suitable for oils and fats, since neutral waxes, although they are completely saponified by alcoholic potash, yield insoluble alcohols and hydrocarbons which interfere with the results. After fats and oils have been saponified, the unsaponifiable matter usually remains dissolved in the soap solution, and it causes turbidity only when a large quantity of it is present. It may be extracted by shaking the solution with ether.

**Procedure.** Weigh out accurately about 5 gm. of the sample, add 12.5 ml. of a 2 N. solution of potassium hydroxide in alcohol and evaporate in a glass dish on a water bath to dryness, stirring at the pasty stage to complete the saponification reaction. Dissolve the resulting soap in hot water, wash it into a 250-ml. separating funnel, and when cool add 50 ml. of ether. Mix the layers by means of combined rolling and inverting motions, so as to avoid the formation of an emulsion which may prove difficult to separate subsequently.

Allow to stand until the two layers separate completely; this separation may be assisted if any emulsion is present by adding 1 to 3 drops (not more) of alcohol. Run off the lower aqueous layer into a beaker through the tap of the funnel, taking care not to lose any drainings from the stem, and pour the top ether layer (which contains the unsaponifiable matter) into a flask through the *top* of the funnel. Return the contents of the beaker to the funnel, and twice repeat the extraction with ether in the above way, using the same beaker. Filter the combined ethereal extracts through a small dry paper into a smaller separating funnel, and shake them with 30 ml. of water, allow to stand, and when separation is complete, run off the bottom layer and pour the top layer into a tared flask. Wash both the paper and funnel with ether.

Distil off the ether (e.g., in an empty Soxhlet apparatus), removing the last traces by blowing air through the flask on the water-bath, and dry the residue for ten minutes in an oven at 105° C. Weigh the residue, and reheat it until the weight is constant. As a precaution the original soap solution should be extracted once again with a fourth portion of ether, which is treated exactly as described above and the extract weighed separately; if extraction is complete, the fourth extract should not exceed about 5 per cent. of the total extracts.

The Table on p. 508 gives the percentages of unsaponifiable matter which are found in a number of normal fats and oils.

*Note.* With a wax, 10 gm. of sample are placed in a dish and 2 gm. of sodium hydroxide dissolved in 2 ml. of water, together with 100 ml. of alcohol, are added. The mixture is evaporated on a water-bath until pasty in consistency, when 10 gm. of freshly-ignited sand and 3 gm. of sodium bicarbonate are added. The mixture is well stirred and heated to dryness. When cool, the coarse lumps are ground to powder, dried in a steam-oven, transferred to a Whatman extractor thimble and extracted with light petroleum (B.P. 40° to 60° C.) in a Soxhlet extractor for two to three hours. If necessary, the mixture may be taken out, dried, ground up again and re-extracted. The extract, which has been received in a tared flask, is evaporated to remove the solvent, and dried to constant weight in the steam-oven.

**Determination of Mineral Oil in the Presence of Saponifiable Oil.** The separation of mineral oil depends on the fact that caustic alkali saponifies only the fatty acids. The mineral oils can be extracted after such saponification by treatment with light petroleum.

Weigh out accurately 10 gm. of the oil into a 200-ml. "resistance-glass" flask. Add 10 ml. of a 50 per cent. solution of NaOH and 50 ml. of alcohol, boil the mixture for thirty minutes in a flask connected with a reflux condenser, and allow it to cool. Transfer the solution to a separator, and shake it with light petroleum (B.P. lower than 80° C.)

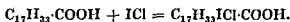
Allow the lower aqueous solution to flow off into another separator and again extract it with fresh light petroleum. Mix the two petroleum solutions

and wash them with 50 per cent. alcohol to extract any dissolved soap; then pour the washed petroleum extract into a beaker, allow it to stand covered for a few minutes to allow any water to settle, and decant the solution into a tared flask. Finally distil off the solvent, dry the residual mineral oil at 100° C., and weigh it. This residue will include the unsaponifiable matter which was present in the vegetable oil, but the amount of this is generally negligible.

### Iodine Value

The Iodine Value is the Percentage of Iodine Monochloride which is absorbed by a Fat or Wax, expressed in terms of Iodine. The process described below is the Wijs modification of the Hübl method. It depends on the fact that unsaturated aliphatic compounds can form additive compounds with the halogens, the extent of this combination depending on their degree of unsaturation. Thus the molecule of oleic acid, which contains one  $C = C$  group, absorbs two atoms of a halogen.

It has been found, however, that in practice iodine is not itself absorbed by such compounds to the extent corresponding with the unsaturation, but that iodine with chlorine (as iodine monochloride) is absorbed quantitatively. In the case of oleic acid, for example, the reaction which takes place is represented by :



The following solutions are required :

(a) *Wijs' Iodine Solution* is prepared by introducing 13 grm. of powdered iodine into a litre flask and shaking them with about 750 ml. of the purest acetic acid, free from  $SO_2$ , until solution is complete, warming on a water-bath if necessary, and diluting the liquid to 1 litre by the addition of more acetic acid. One hundred millilitres of this solution are put aside, and a slow stream of washed and dried chlorine gas is passed into the remainder until the colour of the liquid changes to a clear orange. This change is quite sharp. The iodine solution which was reserved is now added gradually until the orange liquid again becomes distinctly brown, and this solution is heated in a loosely-stoppered bottle in a water-bath for twenty minutes.

Wijs' solution can also be prepared accurately by dissolving 9 grm. of iodine trichloride in a litre of glacial acetic acid (of at least 99 per cent. concentration). The acid must be absolutely free from oxidisable matter, tested as for (d). The halogen content is determined by titrating 5 ml. of the solution against decinormal sodium thiosulphate after the addition of potassium iodide and water. The bulk of the solution is treated with 10 grm. of powdered iodine and shaken to dissolve the iodine, and 5 ml. of this solution are titrated with the sodium thiosulphate as before and the halogen content redetermined; this should be about half as much again as that found in the previous determination. The iodine content is adjusted so that this limit is slightly exceeded, to ensure that no iodine trichloride remains.

(b) *Standard Sodium Thiosulphate Solution* is made by dissolving 25 grm. of the pure thiosulphate crystals in water and diluting the solution to 1 litre. This solution is approximately decinormal, but must be standardised against potassium dichromate (see p. 165).

(c) *Potassium Iodide Solution* is made by dissolving 10 gramm. of the iodide in water and diluting the solution to 100 ml.

(d) *Carbon Tetrachloride* or *Chloroform*, free from oxidisable substances. No green coloration should develop when the liquid is treated with a little potassium dichromate solution and pure sulphuric acid, and the whole heated until the carbon tetrachloride (or chloroform) begins to boil.

**Procedure.** The weight of the sample stated below is dissolved in 5 ml. of the carbon tetrachloride (d), and the solution is placed in a stoppered bottle of about 200 ml. capacity.

From 0.15 to 0.18 gramm. of a drying or marine animal oil.

„ 0.2 „ 0.3 „ „ semi-drying oil.

„ 0.3 „ 0.4 „ „ non-drying oil.

„ 0.6 „ 1 „ „ solid fat.

Fifty millilitres of the Wijs solution (a) are allowed to flow from a burette into the bottle. The mixture is then allowed to stand for at least one hour in a dark place (for two or three hours if the iodine value is very high). In order to avoid loss of iodine, the stopper of the flask is wetted with the solution of potassium iodide (c). The amount of iodine in the liquid is then determined by adding 5 ml. of the potassium iodide solution (c) and 50 ml. of water, taking care to wash down the stopper, and titrating with thiosulphate, using starch solution as indicator.

**Note.** It is essential to add at least three times the volume of Wijs solution that is required to complete the reaction.

A blank experiment, using the same volumes of the reagents in a similar stoppered bottle, should be carried out simultaneously.

**Example.** Determination of the Iodine Value of a sample of lard, the following results

titration, 50 ml. of the iodine solution required 98.5 ml. of the thiosulphate solution. Since each millilitre of thiosulphate solution corresponds with 0.0127 gramm. of iodine, 0.6 gramm. of the lard had absorbed  $(98.5 - 68.1) \times 0.0127$  gramm. of iodine, and 100 gramm. would absorb

$$\frac{30.4 \times 0.0127 \times 100}{0.6} = 64.3 \text{ gramm.}$$

Accordingly the iodine value of the lard was 64.3.

The iodine value of an oil, fat or wax is a constant quantity, but it varies with different kinds of fatty substances. It is therefore of great importance as a means of identifying the substance. The value does not alter materially with the age of an oil, unless some important chemical change, such as oxidation in the case of drying oils and of certain fish-oils, has taken place.

The Table (p. 508) gives the iodine values of various oils and fats, and enables an unknown substance to be classified.

### Soluble and Insoluble Volatile Fatty Acids

The standard tests carried out are the Reichert-Meissl, Polenske and Kirschner values. A full account of these tests together with their interpretation is included in the section on "Butter Analysis" (see p. 385).



### The Hehner Value

The Hehner Value is the Percentage of Insoluble Fatty Acids and Unsaponifiable Matter present in the Fat or Wax. About 3 or 4 grm. of the filtered fat are accurately weighed into a flask and are saponified by boiling for an hour and a half under a reflux condenser with 50 ml. of methylated spirits and 2 grm. of solid potassium hydroxide. The contents of the flask are rinsed into a porcelain dish with boiling water. Saponification is known to be complete when the addition of a drop of water to the liquid no longer produces a turbidity.

The liquid is evaporated until it is pasty, to remove the alcohol; it is then again made clear by adding from 100 to 150 ml. of water, and is acidified by adding dilute sulphuric acid. It is heated until the fatty acids form a clear oily layer, and is filtered through a 10-cm. filter which has been dried at 100° C. and weighed. The filter should be stout enough to prevent the fat from running through and rendering the filtrate turbid, and should have been previously half-filled with hot water. The fatty acids are finally washed on the filter with hot water until the last washing water does not redden blue litmus-paper. The filter with its contents is placed in a weighed beaker and heated at 100° C. for two hours, cooled and weighed. It is again heated for an hour and cooled and weighed, these processes being repeated until the difference between two consecutive weighings is less than 1 mgrm.

Since all natural glycerides contain a small quantity of unsaponifiable matter which is soluble in water, the Hehner value is somewhat greater than the percentage of insoluble fatty acids. The amount of unsaponifiable matter, however, is usually negligible. The insoluble fatty matter in waxes may consist of insoluble fatty acids and insoluble alcohols. This fact and the assimilation of water during saponification may cause the value to exceed 100. The Hehner value, therefore, is not usually determined for waxes, other characteristics being of greater use.

The Hehner values of most oils and fats approximate to 95, butter-fat and some other fats being notable exceptions to this general statement, as is shown in the Table on p. 508.

### The Neutralisation Value and Mean Molecular Weight

The Neutralisation Value is the Number of Milligrams of Potassium Hydroxide which are required to react with One Gramme of the Mixed Fatty Acids. When the saponification value does not exceed 195, the mixed fatty acids obtained in determining the Hehner value (see above) may be considered to represent the total fatty acids present in an oil or fat. If the saponification number exceeds 200, it is best to determine the mean values of the molecular weights of the soluble and insoluble acids separately (see below).

The neutralisation number is obtained by dissolving not less than 5 grm. of the fatty acids in hot neutral alcohol, and titrating the solution with 0.5 N. KOH solution (p. 408). It is necessary to boil the solution just before the end-point is reached, in order to decompose any lactones formed during their preparation.

**Calculation.** If  $M$  represents the molecular weight in grammes of the fatty acids, and  $A$  the number of grammes of KOH required to neutralise 1 grm. of the

fatty acids, then  $M$  grammes of the fatty acids will require 56.1 grm. of KOH for neutralisation, or  $M : 56.1 :: 1 : A$ , and  $M = \frac{56.1}{A}$ .

Or if  $B$  = the neutralisation number, or the number of milligrams of KOH required to neutralise 1 grm. of the fatty acids, then

$$M = \frac{56.1 \times 1,000}{B}$$

**Determination of the Potassium Hydroxide Equivalent of the Volatile or Soluble Fatty Acids.** If the saponification number exceeds 200, and consequently the Reichert-Meissl result is above 5, the volatile fatty acids are present in fairly large quantity, and cannot be determined in the distillate obtained in the Reichert-Meissl process, because only a certain proportion of them distils over. One of the following methods may be adopted. It is assumed that the volatile and soluble acids are identical, an assumption which is true of ordinary fats.

(a) Saponify 5 grm. of the sample with 60 ml. of 0.5 N. alcoholic potash, and determine the excess of potassium hydroxide by titration with 0.5 N. hydrochloric acid (see Saponification Value, p. 409). The weight of alkali used in the saponification represents the saponification value.

Now remove the alcohol by evaporation, dissolve the residual soap in water, add excess of hydrochloric acid to liberate the fatty acids, and wash these acids with water to remove the soluble fatty acids as is described under the determination of the Hehner value. Then dissolve the insoluble fatty acids in neutral alcohol, and determine their neutralisation value by means of 0.5 N. KOH. The difference between this value and the saponification value will give the amount of potassium hydroxide required to neutralise the soluble or volatile fatty acids.

Thus 5 grm. of a butter-fat required 1,130 milligrams of KOH for saponification, and the insoluble fatty acids required 920 milligrams. Hence  $1,130 - 920 = 210$  milligrams of KOH were required to neutralise the volatile fatty acids.

(b) Saponify 5 grm. of the sample in a flask with 60 ml. of seminormal alcoholic potash, and evaporate off the alcohol. Dissolve the residual soap in boiled water and add sufficient seminormal sulphuric acid to neutralise exactly the whole of the alkali taken. The volume of acid required should be determined by a blank experiment in which alkali alone is used, the blank being carried out simultaneously with the saponification of the fat.

Now remove the soluble fatty acids by filtration and subsequent washing, as in Hehner's process; the aqueous filtrate and washings should contain the whole of the soluble fatty acids in the free state, together with potassium sulphate and glycerol. The amount of potash required to neutralise these soluble acids can be determined by titrating this liquid directly with standard alkali, using phenolphthalein as the indicator, and taking the usual precautions against the presence of carbon dioxide.

### The Acetyl Value

The Acetyl Value is the Number of Milligrams of Potassium Hydroxide which are required to neutralise the Acetic Acid obtained by the

**Saponification of One Gramme of the Acetylated Oil, Fat or Wax.** The acetyl value measures the number of alcoholic hydroxyl groups which are present in the original oil. If the glycerides are derived from fatty acids which contain hydroxyl groups in addition to carboxyl groups, then these free hydroxyl groups can also be acetylated. Ordinary fats and oils are practically free from the glycerides of hydroxy-acids, and, unless they have been exposed to atmospheric oxidation, they give acetyl values which are rarely higher than 10, this in part being due to the presence of sterols. Castor-oil, however, gives the very high value of about 100.

Waxes, on the other hand, contain free alcohols which react with acetic anhydride, and the acetyl number of a wax is mainly due to the presence of these alcohols.

Lewkowitsch finds that free fatty acids react upon one another in such a way as to increase the acetyl value, and he accordingly acetylates the original fat or wax instead of the fatty acids. He recommends the following procedure: Boil 10 gm. of the substance for two hours with twice its weight of acetic anhydride in a round-bottomed flask connected with a reflux condenser. Pour the resulting mixture into a large beaker containing 500 ml. of hot water, and boil for half an hour, while passing a slow current of carbon dioxide through the solution to prevent bumping. Allow the mixture to stand and separate into two layers, draw off the water by means of a siphon, and boil the oily layer with three successive portions of fresh water. All the free acetic acid should be removed by this treatment. (Test with litmus to find out whether the last portion of washing water is free from acid.)

Now separate the acetylated fat from the water, and remove the last traces of water by passing the liquid fat through a dry filter-paper, and then by heating it in a drying-oven. Weigh accurately 5 gm. of this acetylated fat and saponify it by treatment with 50 ml. of normal alcoholic potash, accurately measured (see under Saponification Value, p. 409). Evaporate the soap solution nearly to dryness to expel the alcohol; dissolve the residual soap in water, add 50 ml. of normal sulphuric acid (exactly equivalent to the alkali used for saponification), and then 0.5 ml. in excess. Warm the liquid gently until the fatty acids separate as an upper layer. Siphon off the aqueous solution through a wet filter, and wash the fatty acids with hot water until the washing water is no longer acid. Finally titrate the filtrate and washings with decinormal alkali, using phenolphthalein as the indicator. From the number of millilitres of alkali used, less 5.0 ml. (exactly equivalent to the sulphuric acid added in excess), the number of milligrams of KOH which were required for the removal of the acetyl group from 1 gm. of the fat may be calculated.

If the fat or oil contains glycerides of volatile or soluble fatty acids, the value obtained by the above procedure would include the alkali value of the volatile fatty acids. In order to find the *true* acetyl value in such a case, it is necessary to determine the amount of alkali which is required to neutralise any soluble fatty acids which are set free when the acetylated fat, after saponification, is treated with sulphuric acid, and to deduct this from the quantity obtained above.

This may be done conveniently by carrying out a blank experiment on 5 gm. of the unacetylated fat, taking care to use the same volume of water for the final washing as that used to remove the acetic acid.

## Qualitative Colour Tests for Oils

Many colour of tests for oils exist ; the following are satisfactory :

**Halphen's Test for Cotton-seed Oil.** Introduce 2.5 ml. of the oil, or of the liquefied fat, into a strong test-tube, and dissolve it in an equal volume of amyl alcohol ; then add 2.5 ml. of a 1 per cent. solution of sulphur in carbon disulphide. Fit a sound cork into the mouth of the test-tube, and secure the cork by binding a piece of lint over it with twine. Now heat the tube in a water-bath for thirty minutes ; a crimson colour will be produced in presence of 1 per cent. or more of cotton-seed oil or cotton-seed stearin.

An estimate of the quantity of the cotton-seed oil present may be obtained by comparing the colour developed under the same conditions in tubes containing known amounts of the oil, though it should be remembered that all samples of cotton-seed oil do not give the same intensity of colour. Kapok oil is the only other common oil which is known to give a similar colour under the above conditions.

**Baudouin's Test for Sesamé Oil.** Add powdered cane sugar, or 2 drops of a 2 per cent. alcoholic solution of furfural followed by 10 ml. of concentrated hydrochloric acid, to 5 ml. of the oil or melted fat in a test-tube. When the tube is well shaken, a crimson colour will be developed if 1 per cent. or more of sesamé oil is present. In using this test for fat-mixtures, such as butter and margarine, it should be remembered that colouring matters which have been purposely used in manufacture may give a colour with HCl alone ; a blank test should therefore be made, using HCl only, and the result compared with that of the furfural test. This reaction is not given by any other oil.

In certain Continental countries sesamé oil is made an obligatory constituent of margarine, so that if sesamé oil is detected in a fat, the presence of margarine is indicated.

**Bellier's Test for Arachis Oil in a Liquid Vegetable Oil.** The test is suitable for detecting arachis oil in oils, but not in fats. Solid animal and vegetable fats, with the exception of palm-kernel and cocoanut oils, interfere. The following solutions are required :

(a) *Alcoholic Potash.* Dissolve 4.25 gm. of KOH, "pure by alcohol," in 70 per cent. alcohol, and make up to 50 ml.

(b) *Dilute Acetic Acid* of such a concentration that 1.5 ml. will exactly neutralise 5 ml. of solution (a). This is prepared by diluting 14.5 ml. of glacial acetic acid to 50 ml. with distilled water.

*Procedure.* Saponify 1 gm. of the oil in a large test-tube by heating it gently with 5 ml. of the alcoholic potash, and shake the liquid well until it is clear. As soon as the oil is saponified, add 1.5 ml. of the acetic acid and cool the tube in water at 18° C. for not less than thirty minutes. Now add to the solution 50 ml. of 70 per cent. alcohol containing 1 ml. of concentrated HCl per 100 ml. Mix the liquids well and heat the mixture in water at 18° C. for one hour. If arachis oil is present a distinct precipitate will form, even if the sample contains only 5 per cent. of this oil. Other liquid vegetable oils give at most only an opalescence, but usually remain quite clear. Olive oil sometimes gives a

precipitate at first, but if it is then warmed until clear and is placed in water at 18° C. it does not reprecipitate, whereas arachis oil under such conditions will reprecipitate.

**Liebermann-Storch Reaction for Rosin.** Boil a mixture of a few drops of the oil with 2 ml. of acetic anhydride in a small porcelain basin, and filter off the undissolved fat. Place the filtrate in a porcelain basin and allow sulphuric acid of 1.53 specific gravity to drop gently on to the surface of the liquid. If rosin is present, a characteristic violet colour is produced which fades to brown. This test is very delicate. Cholesterol gives a similar reaction, but it is rarely present in fats in sufficient quantity to interfere with the test.

### General Remarks on the Methods and the Results of Analyses

In the examination of an oil, fat or wax, too much stress cannot be laid on the necessity for the greatest care and strictest adherence to the details of the methods employed. In some cases (e.g., the Reichert-Meiss method), empirical methods are used which depend for their success on strict attention to detail, and which give comparable results only when such strict attention is observed.

The methods described will give information sufficient to enable an unknown simple oil or fat to be assigned to the class to which it belongs and in some cases will serve to identify it completely.

If the substance to be examined is a known oil, fat or wax, comparison of the properties and values obtained with those given in the Table (p. 508) will enable its purity to be assessed.

If a mixture of several oils is being examined, the problem is much more complex and difficult, and reference should be made to special books on the subject (p. 519). The interpretation of the results of analysis becomes a matter of weighing up the evidence supplied by each individual test. As Bolton, to whom reference may be made in this connection puts it (*Oils, Fats and Fatty Foods*): "Analytical methods are some of the nature of detective aids to common sense and only a just appreciation of the results will lead to success."

## SOAP ANALYSIS

In an ordinary analysis of soap determinations of water, free combined alkali, fatty acids and insoluble matter will commonly suffice. A more complete analysis would include the free fat, resin, glycerol and certain other substances; and an investigation into the nature of the fatty acids present.

**Preparation of an Average Sample for Analysis.** In preparing an average sample for analysis, great care must be taken, because the water in soap may be distributed throughout the mass, the outside of the sample containing much less than the inside.

*A Bar of Soap* may be sampled as follows: Cut the bar into eight equal parts by three cuts at right angles to each other through the middle of the bar. Take two diagonally opposite eighths and cut them up into twelve equal slices. Mix the slices thoroughly and place them in a stoppered bottle.



with three successive 10-ml. quantities of water. It is then transferred to a weighed 250-ml. flask, the ether is distilled off, the flask is dried in an oven to constant weight and the fatty acids so obtained are weighed.

The aqueous solution and the washings are collected in a beaker, the ether is removed by heating on a water-bath and finally the solution is boiled and reserved for the determination of the total alkali.

**Total Alkali.** All the alkali will be contained in the aqueous filtrate obtained as above. The excess of standard acid is measured by titrating it with standard sodium hydroxide solution. Since a known volume of normal sulphuric acid was originally added to the soap solution, the volume of acid corresponding with the total alkali in the soap can now be obtained by difference, and from this the amount of the combined alkali,  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ , may be calculated.

sample.

**Matter Insoluble in Alcohol.** Place 5 grm. of the average sample in a flat-bottomed dish, and dry them in a vacuum desiccator to constant weight. Dissolve the residue by warming it under a reflux condenser with 100 ml. of 95 per cent. alcohol, which has been neutralised to phenolphthalein by the addition of  $\text{NaOH}$  solution. Filter the solution through a tared filter-paper and wash the residue well with hot alcohol to remove soap, retaining the filtrate in a flask. Dry the paper and its contents at  $100^\circ \text{C}$ ., cool in a desiccator and weigh. This gives the total insoluble matter, both organic and inorganic. The paper may then be ignited in a weighed platinum crucible in order to obtain the inorganic insoluble matter. If the soap contains silicate, the silica may be determined in this residue, or in a fresh portion of the sample (p. 274).

**Free Alkali.** This may be present in the soap either as hydroxide ("free caustic alkali"), or as carbonate, silicate or borate.

"Free caustic alkali" is determined in the filtrate obtained in the above determination. The filtrate is cooled and titrated against decinormal hydrochloric acid, using phenolphthalein as indicator.

The matter insoluble in alcohol (see above) is the free alkali present as carbonates, etc. Dissolve the filter-paper in 150 ml. washing it thoroughly with cold water, solution. Titrate this with decinormal acid, using orange as indicator. If silicate and the alkali found may be as follows:

**Note.** The absolute alcohol is that of carbonate. If also be d. The living The ins  $\text{O}_2$  may

**Resin.** The original Twitchell method depends on the conversion of the fatty acids into their ethyl esters by the action of alcohol in the presence of hydrochloric acid gas. The resin acids under these conditions remain unaltered. This process, however, is a long one, and rather difficult to carry out. It may be replaced conveniently by one of the following methods, both of which depend on a similar principle.

1. *McNichol's Method.* The following solutions are required :

(a) A solution of naphthalene- $\beta$ -sulphonic acid in pure methyl or ethyl alcohol (40 grm. per litre).

(b) A 0.2 N. solution of potassium hydroxide in methyl alcohol.

Two grammes of the mixed fatty and resin acids (p. 419) are dissolved in 20 ml. of the solution (a) in a 150-ml. flask, and boiled gently for thirty minutes under a reflux water-condenser. A blank on 20 ml. of the reagent is carried out at the same time. Both flasks are cooled and the contents titrated with the 0.2 N. KOH, using phenolphthalein as indicator. The difference in the readings is a measure of the resin acids. The mean equivalent weight of the resin acids is usually taken as 346, so that 1 ml. of 0.2 N. KOH is equivalent to 0.0692 grm. of resin acids.

2. *Wolff's Method.* Dissolve 3 grm. of the mixed fatty acids (p. 419) in 20 ml. of pure methyl alcohol, and add 10 ml. of a solution containing one volume of sulphuric acid (sp. gr. 1.84) to four volumes of methyl alcohol. Boil for four minutes under a reflux water-condenser. Cool, add to the liquid five times its volume of an 8 per cent. aqueous solution of common salt, and extract three times with ether. Wash the ethereal extract with salt solution until it is free from acid (to methyl orange). Add 30 ml. of neutral ethyl alcohol and titrate with seminormal potassium hydroxide solution, using phenolphthalein as indicator. The equivalent weight of the resin acids is again taken as 346.

**Potash Soap (Soft Soap).** Since the alkali is present in this soap mainly as potassium oxide, the alkali must be calculated as  $K_2O$  instead of as  $Na_2O$ . If both sodium and potassium are to be determined, the soap is decomposed by hydrochloric acid instead of sulphuric acid, and the alkali metals are determined in the filtrate from the fatty acids by the method given on p. 271.

**The Leeds Scheme of Analysis.** A modification of the scheme devised by Leeds, which aims at carrying out the complete analysis on one sample of soap, is given on the next page.

## MINERAL OILS AND WAXES

Mineral oils and waxes may be divided into two main groups : (1) those found in a natural state in the earth, of which the most important are petroleum and ozokerite ; (2) those produced by the destructive distillation of mineral products, and in particular, shale oils and waxes from shale, and coal-tar oils and waxes from coal.

All these oils and waxes consist of complex mixtures of hydrocarbons. In the process of refinement, they are separated into fractions which distil between certain temperatures, the various fractions being used for widely different purposes. Thus, the oily products obtained in the





fractional distillation of American petroleum may be conveniently divided into three classes : (1) light oils, with boiling-points below  $150^{\circ}\text{C.}$ , used mainly as solvents or as fuel for internal combustion engines ; (2) kerosene or burning oils, with boiling-points between  $150^{\circ}\text{C.}$  and  $300^{\circ}\text{C.}$ , used as oil for lamps or stoves, or in oil engines ; (3) oils with boiling-points above  $300^{\circ}\text{C.}$ , used as lubricating oils, the cruder fractions serving as fuel oil. In addition, vaselin or mineral jelly is obtained, and the residue left behind in the distillation-still consists of pitch. Crude shale oils may be fractionated to give similar products and, in addition, to yield paraffin wax ; the latter is also obtained from certain petroleum and by the destructive distillation of lignite. Coal-tar oils, on fractionation, yield benzols and solvent naphtha, in addition to naphthalene, anthracene, creosote oils, etc. Ozokerite is a naturally-occurring wax which is known as ceresin after it has been refined.

The examination of mineral oils and waxes involves largely the application of physical tests, but a certain number of chemical tests are also employed. The chief physical tests are colour and appearance, specific gravity, range of distillation, viscosity, flash-point, calorific value, "cold test," "cloud test" and "demulsification test"; and, in the case of waxes, melting-point and solidifying-point. For these tests, standard methods have been laid down ; in these, the dimensions of the apparatus to be used and the conditions to be applied are carefully specified. For an account of them, reference must be made to the books listed on p. 520, and also to the *Standard Methods of Testing of Petroleum and its Products*, issued by the Institute of Petroleum Technologists.

The chief chemical tests are for ash, mineral acidity, acid value, saponification value, sulphur content and matter non-volatile above a certain temperature. The mineral acidity is of particular importance in lubricating oils, since such acidity will probably cause corrosion ; a very low acid value, which is a measure of organic acidity, is also required for the same reason. Determinations of the acid value and the saponification value detect oils of a fatty nature. Sulphur in oils is almost always objectionable. In oils, such as white spirit, used in the making of paints and varnishes it may react with the pigments and resins, causing darkening ; in high-grade petrol it is customary to restrict the amount of sulphur because of possible corrosive effects, particularly on the exhaust pipes ; a high content of sulphur in kerosene gives rise to an unpleasant odour on burning ; and in oils used for fuels, although the presence of sulphur is less objectionable, it leads to a distinct diminution in the calorific value and, in larger amounts it may cause corrosion in the cooler parts of the furnace.

An indication is given below of the chief tests to be applied in the examination of various petroleum products.

1. *Petrol*. Specific gravity, distillation-range, mineral acidity. High-grade petrol is also examined for residue on evaporation, sulphur content for the aromatic hydrocarbons content. The "knock rating" is an important test here, as it gives an indication of the probable behaviour of oil in an engine under working conditions.

*White Spirit*. Flash-point, specific gravity and range of distillation, acidity and matter non-volatile at  $100^{\circ}\text{C.}$  Qualitative tests for lead and freedom from grease are also applied.

3. *Kerosene.* Flash-point, colour test, specific gravity and some practical "burning test"; mineral acidity and sulphur content. The most important test is the flash-point, since limits to this figure are laid down by law.

4. *Gas Oils and Oils for Oil Engines.* Specific gravity, calorific value and flash-point; mineral acidity, total acidity and content of hard asphalt (see below).

5. *Lubricating Oils.* These oils are usually examined in great detail, the methods to some extent depending upon the purpose for which they are to be used. The most important test is that of viscosity, since it is a rough measure of the lubricating value. The "cold test" gives an indication of the temperature below which the oil ceases to "run"; if this is unduly high, there is a danger that in cold weather the oil will not flow to the part requiring lubrication. The "cloud test" determines the temperature at which solid wax separates out; wax is harmful since it prevents the free flow of the oil. The "demulsification test" measures the rate at which an emulsion, made of the oil and water, separates out. This test is of importance in testing steam-cylinder and turbine oils. The presence of traces of soaps or alkali salts may cause the emulsion to persist, in which case loss of oil is likely to occur in the cylinder, owing to loss of oil in the steam. The specific gravity is measured, since oils of low specific gravity are preferred for lubrication, other things being equal. The flash-point is a measure of the volatility and in general should be high. Lubricating oils are also tested for their "content of hard asphalt," which is of importance since its presence may lead to resinification, resulting in the clogging of bearing and channels, and the formation of deposits in the cylinders of internal combustion engines. Other tests are for mineral acidity, acid value and saponification value, and iodine value. The last determines rosin, and is used if rosin is detected in any quantity by a qualitative test.

6. *Fuel Oils.* Specific gravity and calorific value; sulphur content.

7. *Paraffin Wax.* Solidifying-point; mineral acidity, acid value and saponification value.

8. *Mineral Jelly.* Flash-point, ash, mineral acidity, acid and saponification values, volatile matter, and melting-point. The last may be determined by observing the temperature at which the first drop of the molten jelly detaches itself from the rest; a special apparatus, of which that of Ubbelohde is an example, is used.

A description of some of the chemical tests is given below. Moisture and ash are determined by the methods given on pp. 406 and 408.

measure of the "total acidity." If the fatty matter present in the oil is known, then the percentage of saponifiable matter is given by :

$$\frac{\text{saponification value found}}{\text{saponification value of the fatty matter}} \times 100.$$

**Non-Volatile Matter** in white spirit, petrol or petroleum jelly is determined by heating 50 grm. of the sample in a shallow flat-bottomed dish on a boiling water-bath for one hour. The dish is dried and cooled in a desiccator and the weight of the residue obtained.

**Sulphur.** The sulphur content of an oil may be determined by burning a known weight of the oil in a bomb calorimeter (p. 324) :

0.5 to 1 grm. of the oil is accurately weighed out into the bomb crucible. If petrol is being used, it should be placed in some form of closed capsule to prevent loss by evaporation during the assembling of the bomb ; the material of which the capsule is made must be free from sulphur. Ten millilitres of distilled water are placed in the bomb itself, the bomb is closed and oxygen is admitted slowly to a pressure of 25 atmospheres. The bomb is immersed in water during the firing of the oil, and is kept there for at least ten minutes after combustion has taken place. The gases are then allowed to blow off very slowly and the bomb cover is removed. The contents of the bomb are emptied into a beaker and the inside of the bomb is carefully washed, the washings also being placed in the beaker. The solution after filtering, if necessary, is diluted until its volume is about 250 ml. ; 2 ml. of concentrated hydrochloric acid and 0.5 grm. of sodium peroxide are added and the solution is boiled. The sulphur, which will have been oxidised to sulphuric acid, is determined in the usual way as barium sulphate (p. 65).

Another method, suitable for petrol or kerosene, consists in burning a measured weight of the oil in a specially designed lamp, and leading the products of combustion through a solution which absorbs the volatile sulphur compounds formed. The sulphur is oxidised to sulphuric acid which is determined in the usual way. For a description of this apparatus, reference should be made to *Standard Methods of Testing Petroleum and its Products*.

**Hard Asphalt.** Five grammes of the sample are dissolved in 200 ml. of light petroleum, which must be free from aromatic compounds and must boil between 40° C. and 60° C. The solution is shaken well and allowed to stand for twenty-four hours in the dark. It is then filtered, either through filter-paper or an alundum crucible, and the residue is washed with the light petroleum until the washings are colourless. The material on the filter is extracted with pure benzene, the solvent being poured through the filter until the runnings are colourless. The filtrate and washings are collected in a weighed flask, the benzene is distilled off on a water-bath, and the flask is dried in a steam-oven for two hours. The flask is cooled in a desiccator and reweighed. The percentage of hard asphalt is calculated from the increase in weight.

## ESSENTIAL OILS

Since essential oils are natural products, their properties may vary over a wide range of values. Determinations of specific gravity, melting-

point, refractive index, optical rotation and chemical numbers follow the lines already described ; additional methods are as follows :—

**Solubility in Alcohol.** Shake 1 ml. of oil in a graduated stoppered 10-ml. cylinder at about 20° C. with 80 per cent. alcohol, which is added 1 ml. at a time, until the drop has dissolved completely. Oils containing no terpenes or sesquiterpenes are usually soluble in less than 5 ml. of alcohol ; old oils, which have started to resinify do not give a clear solution.

**Distillation Tests** are important as a means of detecting adulterants. The oil is separated under reduced pressure (20 mm. of Hg) into ten equal fractions, the boiling-points, refractive indices and odours of which are compared with those of fractions obtained from an oil of known purity.

**Evaluation of Odour.** Drops of oil are spotted on filter-papers, which are placed in a slightly warm atmosphere so that a certain amount of natural "fractional distillation" of the constituents occurs ; the odours are noted from time to time, and in this way two oils may be compared. Since, however, the odours of essential oils are due to the presence of definite compounds, such as esters, aldehydes and ketones, determinations of these individually, though laborious, may provide a better evaluation than an odour test. In addition it is usual to determine specific constituents of certain oils, such as cineole in eucalyptus ; and specific impurities, such as synthetic esters in oil of lavender.

For further details see Allen's *Commercial Organic Analysis*.

# PART VI

## GENERAL ORGANIC ANALYSIS

### SECTION XIV

#### DETERMINATION OF THE ELEMENTS

**Introductory Remarks.** This section describes the most important methods employed for the ultimate analysis of organic substances.

Carbon and hydrogen, the most common constituents of an organic compound, are determined by burning a known weight of the organic substance and determining separately the weight of carbon dioxide and of water which are produced. There is no simple method for determining directly and accurately the percentage of oxygen present, but this is usually calculated by difference after the percentages of all the other constituents have been found.

Several methods for determining nitrogen are described. They are of wide application as they are also used in the analysis of manures and of agricultural products. Methods for the halogen elements, sulphur and phosphorus, are also described.

As in book, are directly or indirectly applicable to their determination in an organic substance.

#### Determination of Carbon and Hydrogen in a Solid Organic Substance

**Organic Combustion Process.** The method followed is a modification of that first described by Liebig. It consists in heating the organic substance to redness in a current of air, and passing the products of combustion through a layer of heated copper oxide whereby the hydrogen is converted into water and the carbon oxidised completely to carbon dioxide. The water is absorbed by calcium chloride, and the carbon dioxide in potassium hydroxide solution or by soda-lime.

**Apparatus for Purifying the Air and Oxygen used in the Combustion.** The apparatus (Fig. 117) consists of: (a) a wash-bottle, (b) a drying-tower, (c) glass tube with tap, (d) a wash-bottle, (e) glass tube with tap.

The air is stored in a gas-holder or in an aspirator over water. It is necessary to arrange the apparatus so that at one period of the combustion the air may be replaced by oxygen, and the most convenient way of doing this is to duplicate the apparatus as regards (a), (b) and (c). The oxygen may be delivered direct from a cylinder, or it may be first transferred to a gas-holder. In the former case, a glass T-piece with one leg dipping into a few centimetres of mercury should be inserted in the drying train in front of (a). This acts as a safety valve and controls

the pressure of the oxygen passing through the apparatus, preventing it rising above a chosen value (see also p. 304).

The wash-bottle (a) contains concentrated sulphuric acid to dry the air. The drying-tower (b) is filled with granules of soda-lime except for about an inch or so at the top, which is filled with anhydrous calcium chloride. This tower removes carbon dioxide from the air, the function of the calcium chloride being to take up any moisture set free from the soda-lime in the process. The tap (c) serves as the main control for regulating the flow of air (or oxygen). The wash-bottle (d) is also filled with concentrated sulphuric acid, but as its chief function is to act as a gauge by which the rate of flow of the air (or oxygen) can be judged,

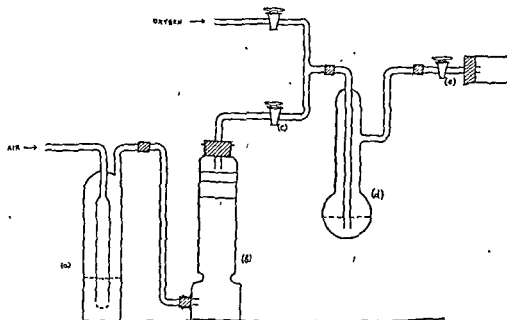


FIG. 117. DRYING TRAIN.

its capacity need not be large. The tap (e) is used for the final adjustment of the air-flow.

Where possible all-glass apparatus should be used. Rubber connections must be as short as possible and tightly-fitting rubber bungs should be used to ensure that the apparatus is free from leaks.

**The Combustion Furnace.** The combustion furnace may be heated either electrically or by gas. A common type of gas-fired furnace consists of an iron framework which supports a sheet-iron trough some 3 feet in length, under which is placed a row of Bunsen burners. The burners are supplied from one gas inlet, but each can be controlled by its own tap. The sheet-iron trough is lined with asbestos tape and on this tape the combustion tube is placed. The framework is so built that rows of fire-brick tiles which meet at the top may be arranged over the combustion tube. When these are closed they serve to concentrate the heat on the tube, and by removing them out of position any part of the combustion tube may be allowed to cool at will.

**The Combustion Tube.** Cut off a piece of combustion tubing, about 1.2 cm. to 1.5 cm. in internal diameter, and long enough to project about 5 cm. from each end of the furnace. Round off the sharp edges at the ends of this tube in the blow-pipe flame and "lip" them slightly so that they may take the rubber stoppers easily. As soon as the glass is cold, cleanse the interior by washing it with a long-stemmed tube-brush in a stream of water, or by attaching a plug of cotton-wool to the middle of a piece of string about 5 feet in length, and drawing the wetted plug up and down the tube; then rinse the tube well in a stream of water from the tap, and dry it by heating it, at the same time passing a stream of clean air through it.

**An Oxidised Copper Coil to prevent Diffusion** is shown at *d* in Fig. 119 (p. 431). This is made by coiling a length of copper gauze tightly around a stout piece of copper

diameter that it fits loosely. The wire are twisted into loops, which enable the coil to be withdrawn from the tube by means of a piece of hooked wire. Before it is introduced into the tube, the coil is repeatedly heated in the blowpipe flame and cooled in the air until it is completely oxidised. During a combustion it is maintained at a red heat, to burn any organic vapour which might diffuse backwards and which would otherwise pass into the purifying train.

**The Porcelain Boat** shown at *e* (Fig. 119, p. 431) must be of such a size that it can readily be pushed into the combustion tube. A platinum boat, *e.g.*, made from platinum foil, may also be used.

**Copper Oxide.** The copper oxide must be prepared by the direct oxidation of metallic copper, usually by roasting short lengths of copper wire in a current of air. If the oxide has been prepared by precipitation or by the ignition of copper nitrate it is quite unsuitable for use in an organic combustion. Suitable copper-oxide wire can be purchased.

**A Silver Coil and Copper Coil.** A cylinder 8 cm. in length, which just passes into the combustion tube, is made by tightly coiling the appropriate metal gauze or sheet (Fig. 119, *g*, p. 431).

The copper coil (see p. 438) should always be used if the substance to be burnt contains nitrogen, and the silver coil when the substance contains a halogen. The copper coil must be treated as described on p. 438 in order to remove copper oxide from its surface. At a red heat the copper deoxidises any nitrogen oxide, and the silver retains any halogen which is evolved during the combustion. These gases would otherwise pass into the absorption tubes, and give rise to errors.

**Lead Chromate.** If the substance contains sulphur, fused lead chromate, in the form of coarse granules, must be substituted for the copper oxide. It is preferable, however, to mix this with copper oxide wire in the proportion of 3 parts of the chromate to 1 of the oxide. In the absence of lead chromate, the sulphur dioxide formed during the combustion would pass on as  $\text{SO}_2$  or  $\text{SO}_3$  into the absorption tubes. In its presence, it is retained as lead sulphate.



**Calcium Chloride Absorption Tube.** The tube *a* (Fig. 118, below), for absorbing the aqueous vapour evolved during the combustion, contains granular calcium chloride, through which  $\text{CO}_2$  has been passed until the weight of the tube has become constant (see p. 87).

*Note.* The greater part of the water which is produced during the combustion collects in the empty bulb on the side-arm of the  $\text{CaCl}_2$ -tube and is emptied out after each combustion as soon as the tube has been weighed. The calcium chloride in the tube is thus prevented from becoming rapidly saturated with water, and one charge may be used for several combustions.

**Soda-Lime Tubes.** These tubes, two of which should be used, are intended to absorb the carbon dioxide which is formed during the combustion. Three-quarters of each tube from one end is filled with granular soda-lime, the remainder of the space being filled with granular calcium chloride. The inlet and outlet tubes are loosely closed by plugs of glass-wool. Reference should be made to the description of the preparation of similar absorption tubes given on p. 87.

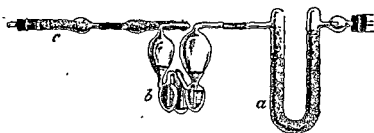


FIG. 118. POTASH-BULBS AND DRYING TUBE.

All tubes and vessels containing absorbent material must be closed from the air, except when they are in use or are being weighed.

**Potash-Bulbs.** Thirty-three per cent. potassium hydroxide solution may be used instead of soda-lime as an absorbent for the carbon dioxide. The liquid absorbent presents the advantage over soda-lime in that the bubbles indicate the rate at which the current of gas is passing. A guard-tube containing granular calcium chloride must be attached to the further end of the bulb apparatus, and must be weighed with it. This tube prevents moisture being carried away from the potash-bulbs during the combustion.

Sodium hydroxide must not be used in these bulbs because the sodium bicarbonate which will then be formed is comparatively insoluble and will crystallise out, so choking the tubes.

The bulbs with their calcium chloride tube are shown in Fig. 118 (*b*). A second, larger, calcium chloride tube (*c*) is attached to the small tube in order to prevent its contents from absorbing moisture from the atmosphere; this tube is removed during the weighing. The potash-bulbs should be recharged after every two combustions.

The Combustion Apparatus is fitted up as follows: About two-thirds (*f*, Fig. 110) of the combustion tube are filled with copper-oxide wire, the pieces being shaken together compactly. The oxide may be kept in its place by means of coiled cylinders of copper gauze placed before and

behind it; each of these cylinders is made by tightly coiling a strip of copper gauze, and is about 2.5 cm. in length and of such diameter that it just passes into the combustion tube.

Sufficient space must be left in the tube for the insertion of the coil (g), and the boat (e), and the diffusion plug (d).

The tube is now laid on the asbestos tape in the iron trough of the combustion furnace, with its ends projecting about 5 cm. from the oven, and perforated discs of sheet-iron or of asbestos board are pushed over the ends of the tube to protect the rubber stoppers from the heat of the furnace. The oxidised copper coil (d) is then introduced.

Two rubber stoppers are now selected to fit the ends of the combustion tube. One stopper is perforated to receive a glass tube of millimetre bore, fitted with a tap (e, Fig. 117), which is connected by a short length of rubber tubing to the purifying train. The other stopper is bored to take the bulb-tube at the end of the calcium chloride tube, and this tube is inserted so that its end is flush with the inner surface



FIG. 119. COMBUSTION TUBE.

of the stopper; the stopper is then pushed into the other end of the combustion tube.

The soda-lime tubes are connected in series with one another and with the calcium chloride tube by means of rubber joints, the soda-lime in each of these tubes being in the limb which is nearer to the  $\text{CaCl}_2$ -tube. The glass tubes are made to touch one another within the rubber joints, which are bound with copper binding-wire if they are not air-tight. Potash-bulbs with a guard-tube may take the place of the soda-lime tubes.

Now proceed to heat the Combustion Tube, containing the copper oxide and the oxidised copper spiral, to redness for at least half an hour with a current of purified air passing through it, in order to remove all combustible matter and moisture. Prove that its contents are no longer evolving carbon dioxide or steam by attaching the absorption tubes, weighed as is described below, and continuing to heat the oxide in the air-current for another half-hour; it should be found that the tubes have not increased in weight during the above process. (*Note.*)

For this purpose, weigh the  $\text{CaCl}_2$ -tube without its rubber caps or connections. As soon as the weighing is finished, slip a little rubber tube, closed with a piece of glass rod, over each of its ends, to prevent access of atmospheric air. Then weigh the soda-lime tubes separately, and immediately close them with similar caps or by turning their glass stoppers; or if potash-bulbs are used, weigh them together with their guard-tube and then close the ends with caps.

Now connect these tubes with one another, and with the combustion tube, and regulate the speed of the current of air passing through the apparatus until the bubbles follow one another through the sulphuric acid (a, Fig. 117, p. 128) at such a rate that they can be easily counted.

Remove the absorption tubes after they have been in connection

with the combustion tube for half an hour, and again weigh them. If any one of them is found to have increased in weight by more than a few tenths of a milligram, the "burning out" process must be continued. Before the tubes are weighed, they should always be allowed to stand for half an hour near the balance-case, in order to reach equilibrium with the atmosphere.

*Note.* The combustion tube and copper oxide need only be tested when a new combustion tube and/or its contents are used, or when the tube has been laid aside for some time. When a series of combustions succeed one another at short intervals, it is unnecessary to carry out the test each time.

For practice in the Combustion Process weigh out accurately into the boat about 0.2 grm. of pure crystallised cane sugar, which has recently been dried in the steam-oven. The boat should have been ignited previously and allowed to cool in a desiccator. Connect the parts of the apparatus together, push in the boat containing the sugar and the oxidised copper coil (*d*). The silver and the copper coils (*g*) may be omitted in this case, because sugar contains neither nitrogen nor halogen.

Make certain that the apparatus is air-tight by stopping up the calcium chloride guard-tube of the potash-bulbs and turning on a slow stream of air. Bubbles will at first be seen passing through the wash-bottles and the potash-bulbs, but the stream should cease when the pressure has adjusted itself. Turn off the air and cautiously release the pressure. Start a slow current of air through the tube and begin to heat the copper oxide (*f*) to redness. The heating is best carried out as follows:

combustion may be completely oxidised.

As soon as the whole of the sugar is burnt, a current of air is allowed to pass slowly for thirty minutes to sweep out the last traces of carbon dioxide and steam, and to displace the oxygen completely from the absorption tubes.

If any water condenses in the end (g) of the combustion tube, it may usually be removed by shifting the screen from the end, so as to allow the whole tube to become gently heated while the air current is passing. All the water must be transferred to the calcium chloride tube by evaporation in the air current. The absorption tubes are detached from the combustion tube and from one another, and their contents are at once shut off from contact with the atmosphere. After they have been allowed

to stand for half an hour near the balance-case, each tube is weighed separately.

The increase of weight of the calcium chloride tube (a) gives the weight of water which has been produced, and the increase of weight of the soda-lime tubes, or of the potash-bulbs with their guard-tube (b) gives that of the carbon dioxide.

... If its weight increases ...  
...  
soda-lime tube.

**Calculation of the Results.** In a particular combustion, 0.2370 grm. of pure sugar was burnt. The calcium chloride tube, which weighed 48.769 grm. before ... 1891 grm. before the combustion,

Therefore the weight of hydrogen in the sugar =  $\frac{0.1382}{9} = 0.0154$  grm. ;

And the weight of carbon in the sugar =  $\frac{0.3655 \times 12}{44} = 0.0997$  grm.

Accordingly the percentage of hydrogen =  $\frac{0.0154 \times 100}{0.2370} = 6.50$  ;

And the percentage of carbon =  $\frac{0.0997 \times 100}{0.2370} = 42.07$ .

The percentage of oxygen is found by difference. These results compare with those calculated from the formula for cane sugar,  $C_{12}H_{22}O_{11}$ , as follows :

	Theoretical.	Found.	Error.
Carbon . . . .	42.10	42.07	- 0.03
Hydrogen . . . .	6.43	6.50	+ 0.07
Oxygen . . . .	51.47	51.43	- 0.04

**The Presence of Nitrogen** in an organic substance leads to the formation of oxides of nitrogen, which would be taken up in the absorption tubes. To prevent this, a copper coil (p. 438) is kept at a red heat in the rear of the combustion tube (Fig. 119, g, p. 431). This coil decomposes any oxides of nitrogen which are produced. The combustion is carried out as above, care being taken that the copper coil is heated to redness before the substance begins to burn. The combustion of the charred substance is finally completed in a current of oxygen.

**The Halogens** present in an organic substance are also evolved during the combustion in a condition in which they may remain in the absorption tubes. They should be completely absorbed by causing them to pass over a red-hot silver coil placed in the tube (Fig. 119, g). The halogens may also be dealt with as follows :

Substances which contain Cl, Br, I, S, and P are usually mixed with lead chromate which has been fused and powdered, instead of with copper oxide, and the combustion tube is filled with granulated lead chromate in place of the copper-oxide wire. The tube and its contents are dried by heating them only to dull redness while a current of dried air is passing ; the chromate must not be fused in this process.

The powdered substance, mixed with about six times its volume of recently heated, powdered chromate, is introduced into the cold tube. The oxidised copper coil is then inserted, the silver coil is placed in the rear of the tube, and the combustion is carried out in a slow current of air. The main portion of the chromate is heated to dull redness, but about 10 cm. of it next to the boat containing the substance must be kept comparatively cool. As soon as the substance is completely charred, a current of oxygen may be passed to complete the combustion.

**A Volatile Solid Organic Compound** must be burnt much more carefully than a non-volatile compound like sugar. The substance must be introduced into the front of the combustion tube after the rear part of the tube has been heated to redness. By cautiously raising the temperature of the tube under the oxidised copper coil, and by reducing the current of air, the substance may be vaporised slowly, the vapour being oxidised in the layer of red-hot copper oxide.

*Note.* If the substance is liable to decompose explosively on heating, it should be mixed intimately with a large quantity of powdered copper oxide and packed into the tube as described on p. 438. The combustion should be carried out cautiously.

Compounds containing alkali or alkaline earth metals should be mixed with 10 parts by weight of powdered lead chromate; otherwise, on decomposition, they may retain a portion of their carbon as carbonate.

### Combustion of Liquid Substances

**A Liquid Organic Substance** which is not very volatile or hygroscopic may be weighed in a boat and burned in the usual way. Or it may be weighed in a small glass tube which is sealed at its lower end, and this may be closed loosely by a stopper consisting of a small piece of glass rod flattened out at the top (Fig. 129, *b*, p. 456), this tube is placed in the boat, and the boat is pushed into the combustion tube.

**A Volatile Organic Liquid** is weighed in a little tube with a capillary opening, and this is introduced into the combustion tube.

The little tube is made by drawing out a short piece of glass quill-tubing to a capillary bore in two parts about 0.6 cm. apart. One of the capillaries is then  
 . . . . . quill-tube  
 . . . . . pressed while  
 . . . . . down the  
 open tube.

First the empty tube is weighed. The liquid is introduced into it in suitable quantity, by heating the tube and allowing it to cool with the end of the capillary immersed in the liquid. The end of the capillary tube is sealed in the flame, and the tube is weighed again. Its gain in weight will give the weight of the liquid which has been taken.

A slight scratch with a file is made near the end of the capillary in order that it may be broken off easily, and the tip is broken off and placed in the boat together with the bulb in such a way that the open end points towards the layer of copper oxide, when the boat is in the combustion tube.

A very Volatile Substance should be weighed in a special tube, from which it may be allowed to escape as vapour into the combustion tube while the liquid is itself outside the furnace. A convenient device, made from a piece of ordinary glass tubing, is shown in Fig. 120. The tube is first weighed empty, and again after the liquid has been introduced and both ends have been sealed. It is then placed either in a dish of cold water, or in ice and salt, according to the volatility of the contents. When the combustion tube has been heated to redness, the horizontal end (a) is opened, and at once pushed through a hole in the bung of the combustion tube. It must fit this hole tightly.

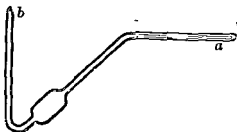


FIG. 120. WEIGHING-TUBE FOR VOLATILE LIQUID.

The temperature of the liquid is allowed to rise and the vapour which will then form passes into the combustion tube and is burned. As soon as the liquid has volatilised, the upright end (b) of the tube is cut off, and air or oxygen is passed through the tube to sweep out all traces of the compound.

Micro-combustion follows the above lines, but the detailed precautions involved are considerable, and reference should be made to Pregl's book on the subject (p. 519).

### Determination of Nitrogen in an Organic Substance

Three general methods for the determination of nitrogen in an organic substance are available.

The Soda-lime Method consists in heating the substance with soda-lime and determining the ammonia which is evolved. This method is limited in application to certain types of compounds, and is now generally superseded by the Kjeldahl method.

The Kjeldahl method depends on converting the nitrogen into ammonium sulphate by heating the substance with pure sulphuric acid, and then determining the ammonia contained in the sulphate. This process, which can be carried out rapidly, is used for the determination of nitrogen in many substances, and especially in manures and vegetable products. It does not give quantitative results with nitro-, nitroso-, azo- and certain other types of compounds.

The Dumas method measures the nitrogen which is evolved when the substance is burned under suitable conditions with copper oxide. This method is of general application.

**Nitrogen by Kjeldahl's Method.** The substance is first heated with pure sulphuric acid, until the carbon and hydrogen are completely oxidised and the nitrogen is converted into ammonium sulphate. The solution is then heated with an excess of sodium hydroxide, and the ammonia evolved is absorbed in a known volume of standard acid and determined volumetrically.

*Sulphuric Acid*, free from ammonium sulphate and from oxides of nitrogen, is required. The purity of the acid can be ascertained by making a blank experiment as is described below, using sugar instead of urea.

**For Practice,** weigh out 0.7 gm. of pure, dry urea or acetanilide into a Kjeldahl flask of about 300 ml. capacity, pour in 20 ml. of sulphuric acid, add 8 gm. of dry, powdered, potassium hydrogen sulphate. Place a small funnel in the neck of the flask, heat the liquid until it is just boiling and maintain it at that temperature in a fume cupboard until the liquid becomes colourless. The potassium bisulphate raises the boiling-point of the acid and thus assists in the decomposition of the organic substance. The addition of a drop of mercury about half the size of a pea accelerates the reaction by catalysis, and is essential with certain complex protein compounds.

All the nitrogen of the urea is converted into ammonium sulphate by this treatment. The ammonia is expelled from this ammonium sulphate and is absorbed in the following way: The cold, acid liquid in the Kjeldahl flask is very carefully diluted with water, transferred to a 500-ml. round-bottom flask, and diluted to about 400 ml.; normal tap water is usually sufficiently free from nitrogen to be used for this purpose. A 5 per cent. solution of sodium sulphide is then added gradually, until the precipitated sulphide of mercury just starts to flocculate. This procedure avoids the retention of nitrogen as nitride, but as it also liberates hydrogen sulphide, an acidic gas, this must be blown out of the flask by means of a clean glass tube attached to a pair of bellows. The colour should then turn to deep black. Place the flask in position for steam-distillation and add carefully down the neck 80 to 90 ml. of 50 per cent. sodium hydroxide solution. Push the flask on to its stopper, and while it is in this position swirl it round to mix the contents, and at once turn on the steam. The distillate contains the ammonia, and is collected in a measured excess of normal sulphuric acid, containing a little methyl orange as indicator, and the excess is titrated with normal sodium hydroxide solution (see p. 134). About 150 ml. should be collected.

From the amount of ammonia obtained the percentage of nitrogen in the urea is calculated.

10.03 ml. of normal sulphuric acid was used in the titration. The volume of acid neutralised by the ammonia was 73.75 ml. The volume of acid remaining was 26.25 ml. The weight of nitrogen in the urea was 0.3675 gm. The percentage of nitrogen in the urea was 46.64.

$$\frac{10.03 \times 250}{34} = 73.75 \text{ ml.}$$

And the volume of acid neutralised by the ammonia was

$$100 - 73.75 = 26.25 \text{ ml.}$$

Now since each millilitre of the normal acid corresponds with 0.017 gm. of  $\text{NH}_3$ , containing 0.014 gm. of N, the weight of nitrogen in the urea was

$$26.25 \times 0.014 = 0.3675$$

And the percentage of nitrogen in the urea

$$= \frac{0.3675 \times 100}{0.788} = 46.64.$$

**Micro-Kjeldahl Method.** This method is strongly recommended as a first exercise in micro-volumetric work, and it does not necessitate a micro-balance; the economies of time and materials are to be noted.

The simplified form of apparatus shown (Fig. 121) is similar in principle to that used for the macro-method. Thus D is the flask for raising steam, K serves the double purpose of a digestion- and distillation-flask; A is the condenser and E the receiver. Urea may again be used for practice, in which case 5 to 10 milligrams will suffice. If a micro-balance is not available 1 or 2 ml. of a 0.5 per cent. solution of urea may be pipetted directly into the flask K, which is 16 cm. long and 1.5 cm. in diameter.

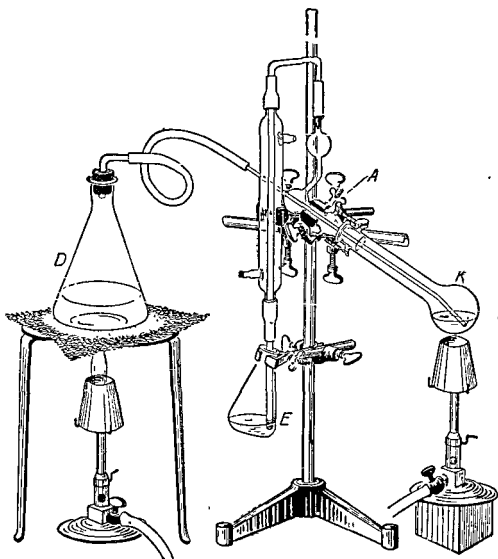


FIG. 121.

Boil off  
10 milligrams  
3 drops of  
about five  
K to the  
K down  
NaOH car  
they run down the side of the flask, and do not meet the acid until K is firmly  
back in position again. The heat generated by the mixture then enables  
distillation to be started at once, and it is complete when in five minutes or less,  
about 60 ml. have collected in E, which should contain, say, 2 ml. of 0.01 N.



$\text{H}_2\text{SO}_4$ . The excess of acid is back-titrated with 0.01 N. NaOH from a microburette. Allowance should be made for a blank experiment on the same quantities of reagents as used.

**Nitrogen by Dumas' Method.** This method depends upon the measurement of the volume of the nitrogen which is evolved by the combustion of the substance. It applies to the analysis of all organic compounds which contain nitrogen.

The organic substance is heated with copper oxide in an atmosphere of carbon dioxide. The constituent elements, nitrogen, carbon, and hydrogen, are then evolved as nitrogen, carbon dioxide, and steam, respectively. These products are passed through a cold, concentrated solution of potassium hydroxide into the measuring-vessel, in which the nitrogen alone collects as a gas. The volume of nitrogen thus obtained is corrected for temperature and pressure, and its weight is calculated.

The determination may be carried out either in an open or in a closed combustion tube.

**Open Combustion Tube.** The following materials are required :

(a) *A Combustion Tube and Furnace.*

(b) *Magnesite* in pieces the size of a pea; or pure, dry *Sodium Bicarbonate*.

(c) *A 25-cm. length of combustion tube sealed at one end.*

This tube is lightly packed with magnesite or sodium bicarbonate, and connected by means of a two-bulbed glass tube with the combustion apparatus, as shown in the diagram. When sodium bicarbonate is used, the tube should

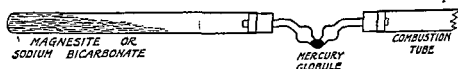


FIG. 122. MAGNESITE TUBE.

be clamped in an inclined position to prevent condensed water falling back on to the hot part of the tube and causing a fracture. The bend in the connecting tube contains a globule of mercury. When the magnesite or sodium bicarbonate is heated, the mercury moves backwards and forwards and gives an indication of the rate at which  $\text{CO}_2$  is being evolved.

(d) *Copper Oxide* in both the powdered and the wire form, freshly ignited.

(e) *A Copper Spiral*, or a *Roll of Copper Gauze*, about 8 cm. in length, and of such diameter as just to fit the combustion tube.

Immediately before use, the surface of the copper must be completely freed from organic matter and from copper oxide. To do this, it is heated to redness in a blow-pipe flame and dropped, while red-hot, into a test-tube containing a little methyl alcohol. The tube, if enfolded in a duster, may be held in the hand. When the alcohol has ceased burning at the mouth of the test-tube and the whole surface of the spiral is brightly metallic in appearance, the spiral is removed and placed in a hard glass tube which is connected by glass tubing through a rubber stopper to a filter-pump. The pump is turned on, the tube is gently warmed and all traces of alcohol are removed by evaporation under reduced pressure. The spiral is then ready to be placed in the combustion tube.

(f) A Schiff nitrometer in which the nitrogen may be both collected and measured (Fig. 123).

It consists of a graduated 100-ml. burette (A) which is supported in a heavy foot and is provided at the top with an accurately fitting stop-cock (c), lubricated with vaselin. The burette is connected by a side tube (a) with a reservoir (B) by means of a flexible rubber tube which has been soaked in melted paraffin wax. A second side tube (b) is connected with the burette at a point about an inch and a half lower down than the first (a) and is inclined upwards. It is fitted with a piece of rubber tubing furnished with a pinch-cock, which enables the side tube to be closed.

Mercury is poured in through the lower side tube (b) until it rises about 1 cm. above the joint, and the tube is closed. The reservoir (B) is charged with a solution of potassium hydroxide, prepared by dissolving the solid in an equal weight of water, the stop-cock (c) is opened, and the reservoir is raised until the potash solution fills the burette. The stop-cock is then closed and the reservoir is lowered and is fixed near the bottom of the burette.

*For Practice in the Process* weigh out 0.15 gm. of pure dry urea. Mix the urea intimately with some of the finely-powdered copper oxide by shaking them together in a stoppered test-tube.

The combustion tube is packed as described on p. 430, except that the mixture of the substance and copper oxide is introduced into the tube at e (Fig. 119) in place of the boat, as follows :

First pour about 2 cm. of powdered CuO through a wide funnel into the combustion tube. Then add the urea mixed with CuO, so that the mixture occupies a length of about 4 to 6 cm. ; rinse out the test-tube with a little powdered CuO, add this to the tube, and finally add a little fresh CuO. The layer of powdered CuO should occupy in all a length of about 10 cm. of the tube. Place the combustion tube in a horizontal position and tap it gently to render the layer compact, but yet loose enough to permit the stream of carbon dioxide to pass readily.

The oxidised copper spiral is introduced at the front end of the combustion tube, the reduced copper spiral at the rear end, and the tube is laid on the bed of the furnace ; the latter should be tilted slightly with the front end raised so as to prevent condensed moisture from running down on to the hot part of the combustion tube.

Connect the combustion tube to the source of the carbon dioxide, and gently heat the magnesite or bicarbonate, whereupon carbon dioxide is evolved and the air driven out of the combustion tube. When nearly all the air has been removed, the rear part of the combustion tube is connected by means of a short length of glass tubing to the side tube (b, Fig. 123) of the nitrometer and the pinch-cock is opened. When only a very minute bubble of air remains from each bubble of gas after it has been "scrubbed" by the solution of potassium hydroxide in the burette, the carbon dioxide which is coming through may be considered free from air.

The reservoir (B) of the nitrometer is then slowly raised to expel the air from the burette through (c) ; this must be done very cautiously so that bubbles of gas continued to pass, otherwise there is a danger of forcing

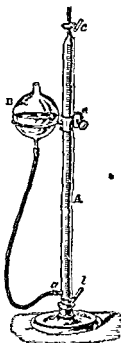


FIG. 123. SCHIFF NITROMETER.

the potash solution through the side tube (*b*) and into the combustion tube. As soon as the burette is free from air and is full of potash solution, the combustion proper may be begun.

This is carried out as described on p. 430. The combustion tube must be heated cautiously, the rate at which the carbon dioxide passes through the nitrometer being controlled to give three or four bubbles per second, and the reduced copper spiral must be red-hot before the substance begins to burn. As soon as the evolution of gas from the urea ceases, the nitrogen must be swept out completely by the current of carbon dioxide.

The gas is allowed to stand in the burette for about an hour, with occasional shaking in order that the absorption of the carbon dioxide may be complete. The reservoir is raised to bring the surface of the liquid in it to the same level as that in the burette, the volume of the nitrogen is read and the temperature of the surrounding air and its pressure are noted.

The volume must be corrected for temperature and pressure, the vapour pressure of the solution of potassium hydroxide being taken as one-half of that of water at the same temperature.

The weight of nitrogen is calculated by means of the following formula (p. 461) :

$$\text{Weight of N} = \frac{v \times (p - w) \times 273 \times 0.001251}{760 \times (273 + t)} \text{ gram.}$$

where  $v$  = volume of nitrogen read in ml. ;  $t$  = temperature of the air ;  $p$  = barometric pressure ;  $w$  = vapour pressure of the KOH solution at  $t^\circ \text{C.}$  ; 0.001251 = the weight of 1 ml. of nitrogen at normal temperature and pressure.

**Closed Combustion Tube.** A combustion tube about 75 cm. in length and sealed at one end is required. The tube is packed as follows : First, a column of magnesite 15 cm. in length, and then, in succession an 8-cm. column of copper-oxide wire, the mixture of substance and powdered copper oxide, a column of copper-oxide wire 30 cm. in length, and the reduced copper wire. The mixture containing the substance is introduced

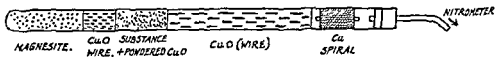


FIG. 124. DETERMINATION OF NITROGEN.

as described on p. 439. The tube is held in a horizontal position and gently tapped to loosen the contents sufficiently to give a free passage to the gases. It is then connected to the nitrometer.

To carry out the combustion, the magnesite is heated until the tube is swept free of air ; the burners underneath it are then lowered, and the wire-worm copper oxide layer in front of the substance and the reduced copper spiral are heated to redness. The burners under the wire-form copper oxide behind the substance are lit and the rest of the combustion carried out as in the open tube. Finally, the magnesite is heated more strongly, in order to sweep out the whole of the nitrogen into the nitrometer.

**Micro-Method.** This follows the above lines, but special precautions particularly in the preparation of the reagents are necessary, and reference should be made to Pregl's book on the subject (p. 519).

### Determination of Chlorine, Bromine and Iodine in an Organic Compound

In all the three methods described the halogen is ultimately weighed as the silver halide.

In the first method, the substance is burnt with lime, or with soda-lime, and the calcium halide produced is dissolved out and precipitated by silver nitrate solution. This method, though somewhat tedious, is of general application, and is to be preferred to the Carius method when two or three halogens are present together in the compound.

In the second method, the substance is decomposed by heating it under pressure with fuming nitric acid in the presence of silver nitrate; in this case the silver halide is produced directly. This (the Carius) method is by far the best when only one halide is present, and, in general, it is more convenient than the first.

The third method, that of Stepanov, is simpler in practice than either of the preceding, but is limited in application. It can be used satisfactorily for compounds which part readily with their halogen, such as halogen substituted aliphatic compounds, but in general it does not give good results with those aromatic compounds in which the halogen atom is very firmly attached to the nucleus.

**Ignition with Lime, or with Soda-Lime.** The powdered solid is mixed with lime or soda-lime (free from chloride or sulphate), and the mixture is heated strongly; the halogen thus combines with the calcium. The cooled mass is dissolved in nitric acid, excess of silver nitrate solution is added to this liquid, and the halogen is precipitated and weighed as silver halide.

The process is somewhat tedious because of the necessity for using a large quantity of nitric acid to neutralise and dissolve the alkaline mass. The filtration and washing of the precipitate and filter are therefore somewhat lengthy.

The quicklime may be readily prepared by breaking marble into small pieces, introducing it into a clay crucible, and heating it strongly in a muffle or in a wind furnace for several hours. The lime thus prepared is removed from the crucible as soon as it is cooled, and is preserved in a well-stoppered bottle. The soda-lime, in a granular condition, is heated strongly to expel moisture, and is stored in a stoppered bottle.

*For practice* weigh accurately about 0.2 gm. of finely-powdered, pure, aniline hydrochloride, or of chloral hydrate,  $\text{CCl}_3\text{CH}(\text{OH})_2$ . Clean a piece of combustion tube, about 50 cm. in length and about 1 cm. in diameter, close one end by drawing it out in the blowpipe-flame, and round off the sharp edges of the open end in the flame.

Fill about 5 cm. of the tube with the powdered lime or soda-lime, and add the weighed substance. Now introduce another 5 cm. of the powdered lime or soda-lime into the combustion tube, and mix the substance with this portion by pushing down into the tube a long, bright piece of wire

which is bent like a corkscrew at its end, and by turning round this wire in the powder and substance. Almost fill the rest of the tube with granular lime or soda-lime, and then insert a loose plug of asbestos.

A volatile organic liquid, in a small tube or bulb with a capillary opening, should be dropped into the combustion tube after the first 5 cm. of lime-powder have been introduced.

Either leave the end of the combustion tube open, or draw it out into a narrow tube which is bent obliquely and which, during the combustion, has its end just dipping below the surface of some water contained in a small beaker.

Now lay the tube in the trough of the combustion furnace, and heat the front portion containing the granular lime to redness. When the lime is red-hot, gradually extend the heat to the mixture. As soon as decomposition is complete, cut off the narrow end of the tube, if it has been drawn off, and transfer the contents of the tube to a beaker. Then rinse out the tube into the beaker with dilute nitric acid (*Note*), add more nitric acid and stir until the lime has completely dissolved. Filter off any particles of carbon and glass, add an excess of silver nitrate solution to the filtrate, and collect, dry, ignite and weigh the precipitate.

*Note.* If iodine is to be determined it is necessary, before precipitating with  $\text{AgNO}_3$ , that sodium sulphite should be added during the treatment of the contents of the tube with nitric acid, to convert any free iodine or iodate into iodide.

**Carius' Method.** The organic substance is mixed with fuming nitric acid and silver nitrate, and the mixture is then heated for several hours in a sealed glass tube. The halogen combines with the silver, and is weighed in this form.

**Procedure.** Cut off a piece of thick-walled combustion tube, a  $\frac{1}{2}$  in. 50 cm. in length and 1.5 cm. in diameter. Seal up one end in the blow-pipe flame, being careful to make the end strong and round in shape. Then anneal the glass well by allowing it to cool down slowly in the reduced flame. This is the digestion tube.

For practice in the process weigh out accurately about 0.2 g. of chloral hydrate,  $\text{CCl}_3\text{-CH(OH)}_2$ , in a small weighed tube about 6 cm. and 8 mm. wide.

If the substance is a volatile liquid, it is sealed up in a small tube (Fig. 120, a, p. 456), or in a thin bulb-tube. The bulb-tube may be made

subsequent use.

Now introduce into the digestion tube about twice as much solid silver nitrate as is theoretically required to react with the halogen. Then pour in 2 ml. of fuming nitric acid through a funnel with a long stem, and push the tube containing the substance into the digestion tube until it rests

on the bottom. The greatest care must be taken to prevent the acid or its vapour from reaching the sample, and if it is contained in a sealed tube or bulb this danger is avoided.

Now draw out and seal the open end of the digestion tube. For this purpose hold it in a slanting position, so that its contents remain undisturbed in their relative positions, and the acid does not reach the substance. Gradually heat the tube at about 10 cm. from its open end, rotating it continually in the flame, until its sides soften and thicken and begin to fall together. Then gradually draw off the upper part, leaving a thick-walled, sealed, capillary end, and carefully anneal this by cooling it first in the luminous flame and finally in the air.

Now place the tube in a loosely-fitting wrought-iron tube and close

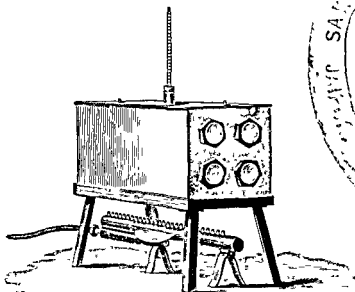


FIG. 125. AIR-BATH FOR HEATING SEALED TUBES.

is with a screw-cap in order to avoid an accident if the glass should  
 vap  
 as  
 the  
 did to mix with the substance in the small tube, or, if the substance  
 has been sealed in a bulb tube, break the bulb by giving the digestion tube  
 a sharp, vigorous jerk, taking care not to splash the acid up into the  
 capillary end. The tube is now ready for heating in the air-bath.

bath, and measures the temperature of the interior. A Fletcher burner suitable  
 for heating the bath uniformly is shown in the figure.

When the bath is in use, a sheet-iron cover which rests upon the upper  
 surface is placed over it. This cover is open at the bottom, and the sides and

ends are half an inch distant from the bath itself. The cover is kept in position by two studs fixed in the upper surface of the bath, which pass through corresponding holes in the top of the cover. This cover helps to maintain a uniform temperature.

When the sealed tube has been enclosed in the wrought-iron tube and the cap has been screwed on, introduce it into the broader tube of the air-bath, place the cover over the air-bath, and light the burner. Allow the temperature to rise slowly, and maintain the bath at the required temperature for several hours by regulating the burner.

A temperature of  $300^{\circ}\text{C}$ . is usually sufficient to ensure decomposition. A lower temperature will frequently serve, and some simple compounds will be decomposed at  $150^{\circ}\text{C}$ .

Allow the bath and tube to become quite cold. The tube enclosed in its protecting wrought-iron jacket is taken out in the jacket, the cap is removed, and the capillary end is slid out of the jacket. Care must be taken not to allow the open end of the iron tube to face the operator, since there may be a very considerable gaseous pressure within the tube, which may cause an explosion. The capillary end is then warmed gently in a Bunsen flame to remove any liquid which may have condensed there, and is then heated carefully until the glass softens and the gas forces an exit and escapes. The tube must on no account be taken out of its wrought-iron jacket before it has been opened.

As soon as the outrush of gas has ceased, the end of the digestion-tube is cut off with a file, and the contents are rinsed out with water into a beaker. If the tube which contained the substance is unbroken, it may be lifted out of the solution by means of a pair of crucible tongs, any silver halide adhering to it being washed back into the beaker. If it is broken, any large pieces of glass are removed and washed. They are then dried in a steam-oven and weighed, the weight of the end which was drawn off during the sealing, if a glass bulb was used, being added. The difference between this weight and that of the original bulb or tube represents the weight of the small pieces of glass which remain in the silver chloride.

The acid liquid is diluted, boiled for a few minutes, and the silver salt is filtered off (*Note*), washed, dried and weighed. The weight of any small glass fragments, which already has been determined, is then deducted, and the true weight of the silver salt is thus obtained; this weight may be checked by dissolving the weighed silver chloride in ammonia, and weighing the residue. From these results the weight of the halogen and its percentage are calculated.

*Note.* If iodine is present in the organic substance, the silver nitrate and silver iodide sometimes fuse together into a yellow mass. The silver nitrate must be removed from this mass by heating it in the diluted liquid for one or two hours.

**Stepanov's Method.** For practice, weigh out accurately 0.2 gm. of chloral hydrate and dissolve it in 40 ml. of 90 per cent. alcohol contained in a 200-ml. conical flask fitted with a water-condenser.

Weigh out roughly 8 grm. of sodium (about fifty times the theoretical quantity of sodium required to complete the reaction), cut it into small pellets and add these, down the condenser tube, to the contents of the flask, so that a vigorous reaction sets in. The sodium should be added at intervals over at least thirty minutes. Boil the solution for an hour.

After cooling, pour 40 ml. of distilled water down the condenser into the flask and distil off the alcohol. Cool the flask again, make the solution acid by means of dilute nitric acid, add 50 ml. of decinormal silver nitrate solution, and, after filtering off the silver halide, determine the excess of silver nitrate volumetrically by means of thiocyanate solution (Volhard's method, p. 197).

### Determination of Sulphur in an Organic Substance

The Sulphur in the Organic Substance is oxidised and converted into Sulphate; it is then precipitated and weighed as Barium Sulphate.

**Oxidation by Nitric Acid**, as in the Carius method for determining the halogens, is suitable for the determination of sulphur. The substance is heated with fuming nitric acid (sp. gr. 1.5) as described on p. 442, the silver nitrate being omitted, and the sulphur is converted into sulphuric acid. When the tube is cold, its contents are transferred to a porcelain dish. An excess of hydrochloric acid is added and the nitric acid is removed by evaporating the liquid nearly to dryness on a water-bath. The liquid is then diluted and the sulphur is determined as  $\text{BaSO}_4$ .

The Methods of determining Sulphur in Coal (p. 319) and in Sulphides (p. 68) also apply to many organic substances.

### Determination of Phosphorus in an Organic Substance

The sample is treated by any one of the processes suggested for the determination of sulphur, the phosphorus being converted into phosphate, which is precipitated with magnesia mixture and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$  (p. 76).



## SECTION XV

### THE DETERMINATION OF MOLECULAR WEIGHTS AND VAPOUR DENSITIES

THE first two methods to be described for the determination of molecular weights apply only to basic or acidic compounds. They depend upon the formation of definite salts, and a knowledge of the basicity of the compound is necessary. In fact, the equivalent weight of the substance is first determined, and the molecular weight is calculated by multiplying the equivalent weight by the basicity.

The third and fourth methods depend on the lowering of the freezing-point or the raising of the boiling-point of a solvent in which the substance has been dissolved; these methods apply to many organic and to some inorganic compounds.

The other methods apply only to volatile substances, and depend on the determination of their vapour densities (p. 454).

#### Determination of the Molecular Weight of an Organic Acid

The Molecular Weight of an Organic Acid may sometimes be determined by preparing an Insoluble Metallic Salt from the Acid, and then by determining the Weight of the Metal in a known Weight of the Pure Salt.

The silver salt is generally selected because it is easily prepared, usually contains no water of crystallisation and requires only to be ignited in order to convert it into the metal. In certain cases the barium or lead salt is prepared and analysed by converting it into the sulphate.

As an example of the use of the silver salt in the determination of the molecular weight of an acid, consider the case of acetic acid. It may be shown by ultimate analysis that the empirical formula of this acid is  $\text{CH}_2\text{O}$ , and it is evident that either this formula or some simple multiple of it will represent the molecule of acetic acid. Also, as only one acetate of the monovalent metals can be obtained, acetic acid is inferred to be monobasic.

The molecular weight of acetic acid may therefore be determined by preparing pure dry silver acetate, and then by igniting a known weight of this salt and weighing the residual silver. The weight of the silver salt which contains 107.88 parts of silver may be calculated from this result. This will be the molecular weight of the silver salt, and, by subtracting from it the atomic weight of silver and adding that of hydrogen, the molecular weight of the acid will be obtained.

**Example.** Two grammes of pure, dry, silver acetate gave on ignition

$$= \frac{107.88 \times 2}{12030} = 166.87.$$

And the molecular weight of the acid

$$= 166.87 - 107.88 + 1 = 59.99.$$

The molecular weight corresponds with the molecular formula  $C_2H_4O_2$ .

**For Practice in the Determination** prepare some pure silver succinate by adding a moderately concentrated solution of silver nitrate to a solution of sodium or ammonium succinate. Filter off the silver succinate, remove dissolved salts from it by washing it with hot water, and dry the salt at as low a temperature as possible.

Now weigh accurately about 1 gram. of the silver succinate into a covered porcelain crucible of known weight, heat it very gently at first, but finally to a red heat for a short time, and weigh it; then repeat the heating and weighing until the weight of the residual silver is constant.

Calculate the molecular weight in the way already described. Since, however, succinic acid is known to be dibasic, it is evident that  $2 \times 107.88$  must be subtracted from the molecular weight of the silver succinate, and  $2 \times 1$  must be added, in order to obtain the molecular weight of the acid.

*Note.* In preparing the silver salt direct from the acid, the latter should be treated with a slight excess of ammonia, and the solution boiled to remove the excess. A neutral solution of the ammonium salt is thus obtained.

### Determination of the Molecular Weight of an Organic Base

Certain Organic Bases, notably the Alkaloids, combine with Hydrogen Chloride and Platinic Chloride to form Double Salts. The constitution of these salts is similar to that of the double chloride of ammonium and platinum,  $2(NH_4Cl) \cdot PtCl_4$ , the organic base taking the place of the  $NH_3$ . The molecule of the double salt therefore, usually contains two molecules of the organic base, and, if R represents a monovalent organic base, the general formula of the double salt will be  $2(RHCl) \cdot PtCl_4$ . When the molecular weight of this organic double salt is known, the value of R can be calculated, since the weight of the other elements present in the molecule is known.

The procedure is identical in principle with that which has been described above. The pure, dry, double salt is prepared, and a suitable quantity of it is weighed; this is then ignited in air until it is free from carbon, and the weight of the residual platinum is determined. Then:

$$\frac{\text{The weight of Pt found}}{\text{atomic weight of Pt}} : \frac{\{\text{weight of double salt used}\}}{\text{molecular weight of double salt}} :: \frac{\{\text{weight of double salt used}\}}{\text{molecular weight of double salt}}$$

The molecular weight of a monovalent base is then found by subtracting from the molecular weight of the double salt the weight represented by  $H_2PtCl_6$ , and dividing the remainder by 2.

**Example.** 2.32 gram. of caffeine platinichloride yielded 0.57 gram. of platinum.

$$\text{Hence the molecular weight of the double salt} = \frac{195.2 \times 2.32}{0.57} = 794.5.$$

$$\text{Therefore the molecular weight of caffeine} = \frac{794.5 - 410.0}{2} = 192.3.$$

**For Practice in the Determination** dissolve some pure caffeine or paratoluidine in dilute hydrochloric acid, and add to the solution a moderate quantity of platinic chloride solution. Filter off the yellow

or orange precipitate of the double salt, wash it with a little cold water and then about six times with alcohol, and dry it in a steam-oven.

Now weigh out 1 grm. of this double salt into a weighed porcelain crucible and heat it, gently at first, and then strongly until all the carbon has burnt away. Then weigh the residual platinum, and repeat the heating and weighing until the weight of the platinum is constant. Calculate the molecular weight of the alkaloid as described above.

### Determination of Molecular Weight by the Freezing-point Method (Raoult)

Both this and the boiling-point method (p. 451) gives approximate results only. On the other hand, the equivalent weight or the empirical formula of a compound can often be determined with great accuracy, and the equivalent weight (or the weight derived from the empirical formula), when multiplied by a small integer, gives the molecular weight. The chief use of these methods is to determine this integer.

These methods are of special value for substances whose molecular weights cannot be determined by the preceding methods, and for compounds which are non-volatile or which decompose on heating. They are not directly applicable to the determination of the molecular weights of compounds which are ionised in solution, nor do they give reliable results unless the solutions used are very dilute.

The freezing-point method depends upon the fact that if the same weights of different, non-ionisable substances are dissolved in equal weights of the same solvent, the respective lowerings of the freezing-point of the solvent are inversely proportional to the molecular weights of the dissolved substances. This depression varies directly with the weight of the substances used and inversely with the weight of the solvent. The depression of the freezing-point of the solvent which occurs on dissolving the molecular weight in grammes of a compound of known molecular weight in a known weight of the solvent is first determined. The molecular weight of any other substance can then be readily found if a known weight of that substance is dissolved in a known weight of the same solvent, and the depression of the freezing-point is noted.

The Formula required for Calculating the Molecular Weight is deduced as follows :

- If  $M$  = the molecular weight of the substance dissolved ;
  - $K$  = the *Molecular Coefficient of Depression*, or the depression of the freezing-point produced by dissolving the molecular weight of the substance in grammes in 100 grm. of the solvent ;
  - $W$  = the weight in grammes of the substance, the molecular weight of which is required ;
  - $S$  = the weight of solvent ;
  - $D$  = the observed depression of freezing-point ;
- Then the depression ( $D$ ) is proportional to the number of gramme-molecules of substance which have been dissolved in 100 grm. of solvent, or to

$$\frac{W}{M} \times \frac{100}{S},$$

hence

$$D : K :: \frac{W \times 100}{M \times S} : 1, \text{ or}$$

$$D = K \frac{W \times 100}{M \times S}, \text{ and } M = K \frac{W \times 100}{D \times S}.$$

The Process of Determination is conveniently carried out in the apparatus of Beckmann (Fig. 126).

The glass tube *A* contains a thin glass stirring-rod and a thermometer *D* reading to hundredths of a degree Centigrade.

The capillary tube of the thermometer usually has a bulbous space at the top, which can receive some of the mercury, and thus enable the height of the mercury thread to be adjusted to suit various freezing-points. The variation in the quantity of mercury present in the stem of the thermometer in different determinations does not affect the accuracy of the result, because only the difference between the freezing-points of the solvent and of the solution, and not the actual temperatures of freezing, is required.

A weighed quantity of the solvent is introduced into the tube *A*, which is then placed in a somewhat wider tube *B*, so that an air-jacket is formed between the tube *A* and the outer vessel *B*. The external vessel *C* contains a stirring-rod and either water or a freezing mixture, the temperature of which must be from 2° to 5° C. below the freezing-point of the solvent. The thermometer is observed while the liquid is constantly stirred. At first the mercury sinks below the true freezing-point, but it rises again as the freezing commences. The highest position of the mercury is read.

When the freezing-point of the solvent has been ascertained from the mean of several determinations, a known weight of the substance, the molecular weight of which is required, is introduced through the side-tube into *A*. The substance is added most conveniently in the form of a pellet, which is made by compressing a suitable weight of the material in a tabloid press. The liquid is then thoroughly stirred until the substance has dissolved, and the temperature of freezing is again noted. The "ice," which consists only of the solidified solvent, will now form at a lower temperature than before, and the difference between the two temperatures gives the lowering of the freezing-point (*D*).

In order to make an accurate determination of the freezing-point, excessive "super-cooling" must be avoided. The final reading should be made by removing the tube from the jacket, and occasionally dipping it into the freezing-mixture and moving it round until the liquid freezes. When this takes place the tube is immediately removed from the mixture and wiped dry. The "ice" will probably have melted by this time, but if not, allow it to do so. Then place the tube in the air-jacket *B* and immerse the latter in the cooling-mixture. Now stir constantly, carefully

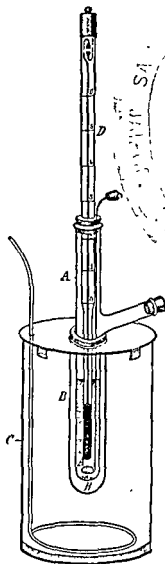


FIG. 126. BECKMANN'S FREEZING-POINT APPARATUS.

observing the freezing, and note down the highest temperature, as has been described above.

The molecular weight (M) is then calculated from the difference between the two freezing-points, by means of the formula given on p. 448.

A series of determinations may be made if necessary, by adding successive quantities of the substance to the same quantity of solvent.

If the Molecular Coefficient of Depression (K) is unknown it can readily be ascertained by dissolving a definite quantity of a substance of known molecular weight in a weighed quantity of the solvent. The value of K is then calculated from the equation on p. 448. The values of K for a few common solvents are :

Water	.	.	.	.	.	.	19° C.
Acetic acid	.	.	.	.	.	.	39° C.
Benzene	.	.	.	.	.	.	49° C.
Phenol	.	.	.	.	.	.	73° C.

For Practice in the Method use 6 grm. of pure cane sugar; dissolve this in 50 grm. of water, for which  $K = 10$ , and introduce a mixture of ice and salt into the outer vessel:

Example. 12.616 gr  
the freezing-point of t  
from the equation on p. 504:

$$\text{The molecular weight} = \frac{K \times W \times 100}{D \times S} = \frac{19 \times 12.616 \times 100}{0.765 \times 92.25} = 340.$$

**Determination of Molecular Weights by the Depression of the Melting-point of Camphor (Rast).** The molecular coefficient of depression of camphor is about 400, and, accordingly, a very small weight of a solid dissolved in it will cause an appreciable depression in its freezing-point.

The melting-point of some pure camphor is determined in the ordinary melting-point apparatus (p. 18) using a thermometer graduated in tenths of a degree Centigrade.

A small, weighed amount of the solid, whose molecular weight is to be determined, is melted together with ten to twenty times its weight (accurately measured) of camphor in a small tube, and the melt is carefully mixed and allowed to solidify. A small portion is then removed, placed in the usual melting-point tube and the melting-tube is again determined. The solid melts to a cloudy liquid in which a "crystalline skeleton" can be detected by the aid of a lens; this melts from the top downwards, and the point at which the last trace is seen is taken as the melting-point. The depression obtained is of the order of 20° to 30° C. The calculation is exactly the same as that for Raoult's method, the coefficient (*K*) to be used being 400. More accurate results are obtained if the molecular coefficient of depression is determined at the same time as the molecular weight of the solid, using a compound (e.g., naphthalene) whose molecular weight is known.

This method has the following advantages. It can be carried out very quickly and very small quantities of solvent and if necessary, a few milligrams only of the solid whose molecular weight is to be determined are required, so that the determination can be carried out on a micro-chemical scale. Again, as the melting-point of camphor is high ( $174^{\circ}\text{C}.$ ),

the ordinary melting-point apparatus can be used, and, owing to the very large depression of the freezing-point, a Beckmann thermometer is not necessary.

### Determination of Molecular Weights by the Boiling-point Method

When a Non-volatile Compound is dissolved in a Definite Quantity of a Solvent, the Boiling-point of the Solvent is raised by an Amount proportional to the Number of Gramme-molecules of the Dissolved Compound.

A convenient and rapid process for the determination of molecular weights of solids by this method is described below. It is a modification by Walker and Lumsden of the Landsberger method. When the vapour from a boiling liquid is passed into another portion of the same liquid which contains a substance in solution, the vapour is condensed in the solution, and its latent heat of vaporisation raises the temperature of the solution to its boiling-point.

This principle is applied in the method which is described below. The vapour from the boiling liquid is first passed through another portion of the liquid until the boiling-point is constant. The temperature is observed and a weighed quantity of the substance whose molecular weight is to be determined is added. The vapour of the solvent is passed in again until the substance is dissolved and the boiling-point of the solution is constant. The thermometer bulb must be immersed in the solution, as the vapour is at the temperature of the boiling-point of the solvent, which is lower than that of the solution.

Either the weight or the volume of the solution is now determined. In practice it is more convenient to measure the volume of the solution at its boiling-point and to deduce its weight from this volume.

From the weight of the solution thus determined and the elevation of the boiling-point of the solvent, the molecular weight of the substance can be calculated. In the arrangement devised by Landsberger the escaping vapour forms a jacket round the boiling solution; the errors arising from superheating and radiation are thereby largely reduced.

The Apparatus is shown in Fig. 127. It consists of a bulbed, inner vessel (A), which contains the solution of the substance. This vessel is connected by tubes (BC) with a flask (D) containing the solvent to be boiled. The vapour from this flask passes to the bottom of the vessel (A) and then up through the solution to escape by the hole (E) into the jacket (F) and

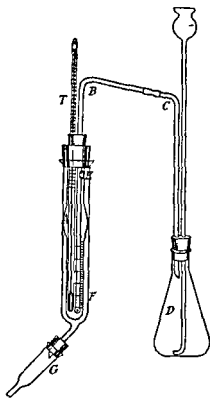


FIG. 127. MOLECULAR WEIGHT BY ELEVATION OF BOILING-POINT.

thence into the condenser (*G*). The inner vessel (*A*) is graduated in millilitres and contains a thermometer (*T*) the stem of which is divided into tenths or less of a degree Centigrade. In order to secure uniform and regular boiling of the liquid in the flask (*D*) a few pieces of unglazed tile are introduced, and a fresh piece of tile is added each time boiling is recommenced.

**The Method.** Place from 5 to 10 ml. of the solvent in the vessel (*A*) and about 150 ml. of the solvent together with a few pieces of unglazed tile in the flask (*D*). Connect the parts of the apparatus as is shown in the figure, and boil the liquid in the flask. The vapour will pass into the vessel (*A*) and will quickly raise the temperature of the solvent to the boiling-point. When the temperature becomes constant, read the thermometer to one hundredth of a degree by means of a lens. This temperature is the boiling-point of the solvent. The thermometer should be tapped gently just before the reading is taken.

Disconnect the tubes (*BC*) and pour out all but 10 ml. of the condensed solvent from the vessel (*A*). Introduce from 0.5 to 1 gram. of the substance into the vessel, place a fresh piece of tile in the liquid in the flask (*D*), connect the tubes (*BC*) as before, and start boiling the liquid again. The thermometer will rise rapidly, and will remain approximately constant at a temperature a little higher than the boiling-point of the solvent. The boiling-point of the solution will then fall slowly but continuously as the quantity of liquid in the vessel (*A*) increases by condensation of the vapour.

As soon as the highest temperature has been attained, read the thermometer accurately, stop the boiling in the flask, disconnect the tubes (*BC*), remove the cork with the tube and thermometer, and quickly read the volume of the solution. The boiling-point of the solution is thus determined, and the difference between this boiling-point and that of the solvent gives the rise of boiling-point which is due to the presence of the substance.

Further determinations should be made by using the solution already present in the vessel (*A*). For the purpose a fresh piece of tile is placed in the flask (*D*) and the boiling is started again. After two or three minutes' boiling, readings of temperature and of volume are taken as before. These operations are repeated, and several determinations of the molecular weight can be obtained in this way with the same quantity of the substance in the course of half an hour.

The Methods of Calculating the Molecular Weight from the volume and the weight of the solution are shown below.

If  $w$  = the weight of substance dissolved ;

$V$  = the volume of the solution in ml. ;

$D$  = the elevation of boiling-point observed ;

$K'$  = the elevation for 1 gramme-molecule of substance dissolved in 1 ml. of solvent ;

$M$  = the molecular weight of the dissolved substance ;

Then since there are  $\frac{w}{M}$  gramme-molecules in  $V$  ml. of solution, there will

be  $\frac{w}{MV}$  gramme-molecules in 1 ml. of solution.

If the elevation for 1 gramme-molecule in 1 ml. of solvent =  $K'$ , then the elevation for  $\frac{w}{MV}$  gramme-molecules

$$= \left( \frac{w}{MV} \right) \times K' = D,$$

whence 
$$M = \frac{K'w}{WD} \quad (1).$$

On the other hand, if the solution is weighed each time, the following formula is arrived at by a similar process of reasoning :

$$M = \frac{Kw}{WD} \quad (2),$$

where  $K$  = the elevation for 1 gramme-molecule of solute in 1 gram. of solvent, and  $W$  = the weight of the solvent.

The values of  $K'$  and  $K$  for different solvents are as follows :

Solvent.	$K'$ .	$K$ .
Alcohol . . . . .	1615	1100
Ether . . . . .	3100	2160
Water . . . . .	520	520
Acetone. . . . .	2300	1730
Chloroform . . . . .	2730	3850
Benzene . . . . .	3105	2600

Note that  $K = K'S$ , where  $S$  is the specific gravity of the liquid solvent at its boiling-point.

For Practice in the Method about 0.5 to 1 gram. of the substance, according to its solubility, should be used. The following substances and solvents will be found suitable: Urea in water; benzoic acid in absolute alcohol; naphthalene in chloroform; camphor in acetone.

Example. 0.829 gram. of camphor was dissolved in acetone. The series of four successive observations, made by passing the vapour of boiling acetone into this solution were as follows :

Number of Experiment.	1	2	3	4
Elevation of boiling point in degrees Centigrade .	1.47	1.09	0.71	0.64
Volume of solution in ml. .	8.1	10.7	16.7	19.0

From the first experiment the molecular weight

$$= \frac{2220 \times 0.829}{1.47 \times 8.1} = 155,$$

and from the subsequent experiments the values are 158, 153, and 151, respectively. The average of these four values is 151.8, a number approximating to the value 152 calculated from the molecular formula.



## VAPOUR DENSITY DETERMINATIONS

**Introductory Remarks.** By the term "vapour density" is usually meant the density of a vapour referred to that of hydrogen as unity.

Hydrogen is selected as the standard instead of air for the following reason. According to Avogadro's hypothesis, equal volumes of all gases and vapours under the same conditions of temperature and pressure contain an equal number of molecules, and, because the molecule of hydrogen contains 2 atoms, it follows that the molecular weight of a gas or vapour is equal to twice its vapour density compared with hydrogen as unity. The molecular weight in grammes of any substance occupies 22.4 litres at normal temperature and pressure (p. 461). In the determination of vapour density, either the weight of a given volume of vapour (or gas) or the volume of a given weight of substance in the form of vapour is found, and from this, by calculation, the weight in grammes of the substance which occupies 22.4 litres at normal temperature and pressure. This is the molecular weight, and one-half of it is the vapour density.

For determining the vapour density of a volatile compound, the method commonly employed is that due to Victor Meyer. The apparatus for this method is simple and easy to use; furthermore, only a small weight of the compound is required.

The method of Dumas is more complicated in every respect, and requires more of the compound.

Of other methods which are available, that of Hofmann may be mentioned. In this method, a small known weight of the compound is vaporised in the Torricellian vacuum above the mercury in a long closed tube, and the volume and pressure of the vapour are measured. This enables the vapour density of a substance which decomposes at its boiling-point under atmospheric pressure to be determined, since the pressure under which it vaporises in this apparatus is considerably below that of the atmosphere. As the method, however, is rather cumbersome and numerous corrections are required for an accurate result, it is seldom used. For details, refer to the special books mentioned on p. 519.

## The Victor Meyer Vapour Density Method

This method determines the volume of the vapour which is produced from a known weight of a volatile substance, by measuring the volume of air displaced when the substance is vaporised.

The volume of the displaced air is measured in millilitres at atmospheric temperature and pressure, and while saturated with aqueous vapour; and from this result the volume of the air when dry and under normal conditions is calculated. This volume would be that occupied by the given weight of the substance, provided that it could be vaporised at normal temperature and pressure.

By calculation, the weight in grammes of the substance which would occupy 22.4 litres is obtained. This is the molecular weight, and the vapour density is equal to one-half of this figure.

The Apparatus is shown in Fig. 128.

The inner tube (b) is long and narrow, and is enlarged into a cylindrical bulb at the base. The whole tube has a capacity of about

200 ml., and is somewhat broader at the top so that it can be closed by the insertion of a tightly-fitting cork. A short distance below the top a bent capillary delivery tube (*c*) enters at right angles.

A broad outer tube (*a*), which is enlarged into a bulb at the bottom, serves as a heating-jacket for the inner tube. A liquid, which has a much higher boiling-point than that of the liquid whose vapour density is to be determined, is placed in the bulb of this jacket.

Water is frequently used in the outer jacket, but substances of higher boiling-point than water, such as xylene, aniline or sulphur, are sometimes required. If the design of the outer jacket is suitable, this jacket need contain nothing but air; when very high temperatures are required, the inner tube may be made of porcelain and be immersed in molten lead.

A measuring-tube (*d*), about 100 ml. in capacity and graduated in fifths of a millilitre, is filled with water and is inverted in a vessel of water. This stands at a convenient height for collecting the air escaping through (*c*).

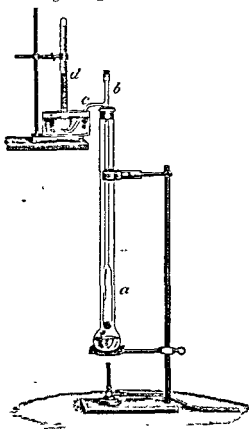


FIG. 128. MEYER'S VAPOUR DENSITY APPARATUS.

**The Procedure.** For practice in the method, the vapour density of ether may be determined as follows:

The apparatus is fitted up as is shown in Fig. 128. A layer of sand or dry asbestos is placed on the bottom of the cleaned and dried inner tube and the top of the latter is closed by a rubber bung. The bulb of the jacket-tube is then half-filled with water, and the inner tube is fitted centrally into the mouth of the outer tube by pressing in the two halves of a bisected cork, in which small openings have been made for the escape of steam. The collecting trough is arranged at such a height that the curved end of the delivery tube dips beneath the water when the apparatus is in position. The water in the outer tube is then heated to boiling, and is kept boiling vigorously by a Bunsen burner, so that steam surrounds the vapour-tube completely and escapes through the cork in the top.

As soon as no more air bubbles escape from the delivery tube (*c*) through the water in the trough, the bung is loosened in the top of the inner tube, since the air within it will have reached steam-heat and the tube is therefore ready for the determination. The measuring-tube (*d*) is filled with water and clamped in position over the end of the delivery-tube (*c*). It is

preferably clamped at an angle of  $45^\circ$  rather than held vertically as shown in Fig. 128.

Meanwhile a little glass tube about 3 cm. in length is made out of quill-tubing, one end being closed and the other being drawn out to a capillary. The tube is shown drawn to actual size in Fig. 129, *a*. The tube is weighed, and is then heated, in pure ether until .. The tube is then re- of ether taken.

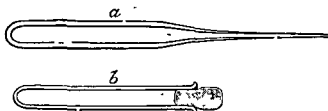


FIG. 129. WEIGHING-TUBES.

The little glass tube for containing the weighed liquid may be furnished with an accurately-fitting small stopper (Fig. 129, *b*). This is made by grinding a piece of glass rod into the mouth of the tube with wetted emery-powder or carborundum. The necessity of making a fresh tube for each determination is thus avoided.

The tube containing the ether is then at once dropped into the inner tube, which is immediately closed by the bung. The ether will vaporise at once, and its vapour will displace air from the inner tube. This air will escape in a stream of bubbles into the measuring-tube. As soon as no more bubbles are seen, the cork of the inner tube (*b*, Fig. 128) is removed.

The measuring-tube (*d*) is then lifted in a ladle full of water, and is transferred to a tall cylinder of water, which should be at the temperature of the air. The tube is wholly immersed in the water, and as soon as its contents have attained the temperature of the water the tube is raised until the water-levels inside and outside are the same. The volume of the air is then read carefully, and the temperature of the water and the barometric pressure are noted at the same time.

**Calculation of Results.** If,

$S$  = the weight of substance taken.

$t$  = the temperature of the water in the cylinder in  $^\circ\text{C}$ .

$v$  = the observed volume of the air in ml.

$p$  = the barometric pressure.

$w$  = the pressure of water at  $t^\circ\text{C}$ .

The observed volume corrected to "N.T.P." (p. 461).

$$= v \times \frac{273}{273 + t} \times \frac{p - w}{760} \text{ ml.}$$

This is the volume occupied by  $S$  grm. of substance.

$\therefore$  22400 ml. would be occupied by

$$\frac{S \times 22400 \times (273 + t) \times 760}{v \times 273 \times (p - w)} \text{ grm.}$$

This expression is the gramme-molecular weight of the substance, and one-half of this value is the vapour density.

**Example.** In a determination of the vapour density of ether, the following numbers were noted down :

Weight of ether taken	= 0.073 grm.
Temperature of water	= 21.5° C.
Volume of air displaced	= 25.3 ml.
Barometric pressure	= 748.0 mm.
Pressure of aqueous vapour	= 10.07 mm.

Hence the molecular weight

$$= \frac{0.073 \times 22400 \times (273 + 21.5) \times 760}{25.3 \times 273 \times (748.0 - 10.07)} = 72.61,$$

and the vapour density = 36.30.

### The Dumas Vapour Density Method

In this method the weight of a definite volume of the vapour of the substance, measured at a known temperature and pressure, is determined. The volume which the vapour would possess, if it could exist under normal conditions of temperature and pressure, is calculated from this result, and hence the molecular weight and the vapour density can be determined.

The Apparatus is shown in Fig. 130. A large thin glass bulb, with its neck drawn out, is used for containing the vapour; it has a capacity of about 200 ml. Such a bulb may be purchased, or it may be made by

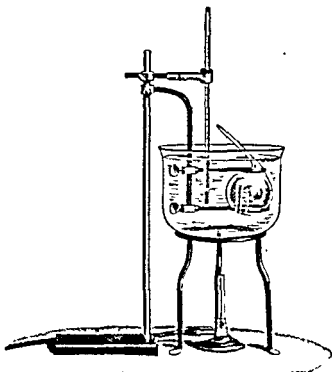


FIG. 130. DUMAS VAPOUR DENSITY APPARATUS.

drawing out the neck of a round flask. After the liquid has been introduced, the bulb is supported in a double clamp, and is immersed in a suitable liquid contained in a large vessel. A copper water-bath, placed

on a tripod stand and heated by a gas burner, serves the purpose well. The temperature of the liquid in the bath is measured by means of a thermometer, the bulb of which is placed near the middle of the vapour-bulb.

**The Procedure.** For practice in the method, the vapour density of benzene may be determined as follows :

The empty apparatus having been arranged as is shown in the diagram, the bulb, together with its clamp, is removed. The bath is then nearly filled with water, which is heated to boiling. Meanwhile, the clean dry bulb is placed in the balance-case for half an hour and is then weighed. About 20 ml. of pure benzene are introduced into the bulb by heating the bulb and allowing it to cool with its open end immersed in the benzene.

The bulb is fixed in its clamps and is immersed in the gently-boiling water in the bath, with the end of the tube projecting about 2 cm. above the surface of the water. The bulb is clamped in this position. The thermometer is also put in at once, with its bulb level with the middle of the vapour-bulb and close to it.

The benzene will boil vigorously, and the vapour which it evolves will pass out from the neck and expel the air from the bulb. When the vapour has issued for some time and begins to escape more quietly, it may be kindled at the end of the tube, and the dropping of the flame will show when the escape of vapour ceases. Then the end of the tube is sealed at once by a blowpipe-flame. At this moment the temperature shown by the thermometer immersed in the bath and the barometric pressure are read.

The bulb is removed from the bath and is dried and allowed to cool. It is placed in the balance-case for half an hour and is then weighed, together with the small piece of glass which may have been drawn off when the bulb was sealed. The temperature inside the balance-case is noted.

A file-scratch is made near the sealed end of the tube of the bulb, and the end is broken off under water which has been recently freed from air by boiling and rapid cooling. The water in the bulb is then transferred into a graduated measuring-cylinder, and the volume of the water, together with that of any air bubble which was in the bulb, will give the capacity of the bulb (*Note*). The water may be weighed instead of being measured volumetrically, and its volume may then be calculated.

*Note.* If the residual bubble of air is of appreciable size, a correction for it must be made in the weight and in the volume of the vapour (*G*), and in the weight of the hydrogen.

#### Calculation of Results. Let

$g$  = weight of dry empty bulb containing air.

$G$  = weight of bulb filled with vapour.

$t$  = temperature of air in the balance-case.

$T$  = temperature of bath at the time of sealing the bulb.

$p$  = barometric pressure, in mm. of mercury.

$c$  = volume of bulb, in millilitres.

The bulb when weighed initially was full of air ; at the final weighing it was full of vapour.

Hence  $G - g$  is the difference in the weights between  $c$  ml. of vapour, measured at  $T^\circ \text{C.}$  and  $p$  mm. pressure, and  $c$  ml. of air measured at  $t^\circ \text{C.}$  and  $p$  mm. pressure. Corrected to normal temperature and pressure these become :

$$c \times \frac{273}{273 + T} \times \frac{p}{760} \text{ ml. for the vapour,}$$

and  $c \times \frac{273}{273 + t} \times \frac{p}{760} \text{ ml. for the air.}$

Let these corrected volumes be denoted  $v$  and  $a$ , respectively. It is known (p. 516) that 1 grm. of air at normal temperature and pressure occupies 773 ml. Therefore the weight of the air is  $\frac{a}{773}$  grm. and the weight of the vapour is  $G - g + \frac{a}{773}$ .

This weight occupies  $v$  ml. at normal temperature and pressure. Hence the weight of 22400 ml. of the vapour is

$$\frac{\left(G - g + \frac{a}{773}\right) 22400}{v} \text{ grm.}$$

This is the molecular weight of the vapour, and one-half of this expression is the vapour density.

**Example.** In a determination of vapour density,

Weight of the bulb	= 23.683 grm.
Apparent weight of the bulb + vapour	= 23.957 grm.
Temperature of air	= $16^\circ \text{C.}$
Temperature of bath	= $112^\circ \text{C.}$
Barometric pressure	= 755 mm.
Capacity of bulb	= 180 ml.

Therefore the corrected volume of the vapour is

$$180 \times \frac{273}{273 + 112} \times \frac{755}{760} = 126.8 \text{ ml.}$$

and the corrected volume of the air is

$$180 \times \frac{273}{273 + 16} \times \frac{755}{760} = 168.9 \text{ ml.}$$

Hence the molecular weight of the compound is

$$\frac{\left(23.957 - 23.683 + \frac{168.9}{773}\right) 22400}{126.8} = 87,$$

and the vapour density is 43.5.

## PART VII

# GAS ANALYSIS

### Introductory Remarks

WHEN the volumes of gases are measured under different conditions, corrections must be applied to the results in order to make them comparable one with another. These corrections are rendered necessary by the appreciable effect which changes of temperature and pressure, and the presence of varying amounts of moisture exert upon the volume of a gas.

The methods for measuring and analysing gases, which are described in detail in this Section, involve the use of comparatively cheap and simple apparatus. They also either dispense altogether with the use of mercury, or require it only in small quantity.

The volume of a gas is frequently measured over water. This introduces a certain amount of error, since gases are soluble in water in varying degree. The results obtained are therefore somewhat less accurate than those obtained when the gases are measured over mercury. The simpler method of measurement over water is generally adopted for certain gases, and is found to give satisfactory results when a suitable volume of gas is employed and proper precautions are taken. The error caused by the solution of the gas in the water may often be reduced by previously saturating the water with the gas which is to be determined. Other alternatives to mercury which have lower solvent powers for most gases than has water are 50 per cent. glycerin, 22 per cent. sodium chloride or concentrated calcium chloride solutions; they are, however, rather unpleasant to handle.

For the description of the larger and more costly forms of gas apparatus, and for directions regarding their use, reference may be made to the books on gas analysis mentioned on p. 519.

## SECTION XVI

### CALCULATION OF NORMAL VOLUME. CALIBRATION OF MEASURING-VESELS

#### Calculation of Volume under Normal Conditions

THE volume of a definite weight of a gas varies appreciably with comparatively small changes in temperature and pressure. If the gas at constant pressure is brought into contact with water, the volume is also increased by the introduction of aqueous vapour.

The volume of a gas is usually measured at the temperature of the laboratory and at atmospheric pressure. Since, however, the temperature and atmospheric pressure within the laboratory are subject to variation, the conditions under which different measurements of gas are made will also vary. Again, the gas may sometimes be measured while it is standing over water, and at other times while it is over some non-volatile liquid; the gas may accordingly either be saturated with water vapour, or it may be dry, and these differences will affect its volume.

In order to make the volumes of gases measured under different conditions comparable with one another, and to be able to calculate the weight of a given volume of a gas, it is therefore necessary to determine the volume which the gas would occupy in the dry state and at 0° C. and 760 mm. pressure. This is usually termed "the volume under normal conditions," or the volume at "N.T.P."

**Calculation of the Volume of a Gas under Normal Pressure.** The volume of a gas varies inversely as the pressure which is exerted upon it. Hence, if

- $v$  = the observed volume of the gas ;
- $p$  = the observed barometric pressure ;
- $V_n$  = its volume at 760 mm. pressure (normal) ;

$$\text{Then } V_n = \frac{p \times v}{760}.$$

This formula supplies the "Correction for Pressure."

**Calculation of the Volume of a Gas at Normal Temperature.** If the pressure is kept constant, a gas expands or contracts by one two-hundred and seventy-third ( $= 0.003665$ ) of its volume at 0° C., for each degree Centigrade rise or fall in its temperature. Hence, if

- $v$  = the observed volume of the gas ;
- $t$  = the observed temperature ;
- $V_0$  = its volume when reduced to 0° C. (normal) ;

$$\text{Then } V_0 = \frac{273 \times v}{273 + t} = \frac{v}{1 + 0.003665t}.$$

This formula supplies the "Correction for Temperature."

**Calculation of the Volume of a Gas in the Dry Condition.** When equal volumes of gas are saturated with aqueous vapour at the same temperature,



they always contain the same quantity of water vapour. The quantity of vapour present increases as the temperature rises and decreases as the temperature falls.

The water vapour which is mingled with the gas exerts a certain pressure which varies with the temperature, and this pressure, which is usually expressed in millimetres of mercury, has been very accurately determined for each degree of temperature (see Table on p. 499).

The pressure of aqueous vapour acts in opposition to the barometric pressure, and tends to increase the volume of a gas. Hence correction is made for its effect on the volume of the gas by subtracting the vapour pressure from the barometric pressure. Thus if  $w$  is the pressure of aqueous vapour in a volume of moist gas under pressure  $p$ , the true pressure of the gas =  $(p - w)$ .

**General Formula for the Calculation of the Volume of a Gas under Normal Conditions.** The preceding corrections are combined into one expression in the following formulæ, in which  $V$  represents the volume of the dry gas at normal pressure and temperature, after correction for saturation with moisture if necessary :

1. For a dry gas,

$$V = \frac{p \times 273 \times v}{760(273 + t)} = \frac{p \times v}{760(1 + 0.003665t)}$$

2. For a moist gas,

$$V = \frac{(p - w) \times 273 \times v}{760(273 + t)} = \frac{(p - w) \times v}{760(1 + 0.003665t)}$$

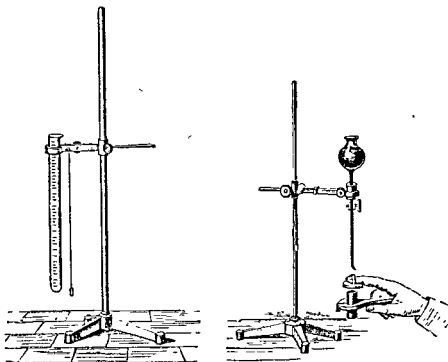
### Calibration of Measuring-tubes

Tubes for the measurement of gases are graduated either in millilitres and fractions of millilitres, or in millimetres, along the length of the tubes. If the latter system has been chosen, the value of each graduation in terms of millilitres must be determined. A glass tube frequently varies in diameter in different parts, and equal lengths on different parts of a graduated tube do not necessarily correspond with equal capacities. It is therefore usually necessary to calibrate the tube throughout its length. Mercury or water is commonly used for calibrating measuring-tubes.

**Calibration of the Measuring-tube by means of Mercury.** The tube is supported vertically with its open end upwards, and successive equal weights of mercury are poured into it from a little tube about 4 ml. in capacity. The space in the tube which is occupied by each portion of mercury is noted by means of the graduations, and the volume of the mercury added is then calculated from its weight. The capacity of the tube at every graduation can then be determined by calculation.

*Calibration of the Measuring-tube used in Meyer's Vapour Density apparatus (p. 455).* Fix the clean tube in a wooden clamp and make it truly vertical by hanging a plummet beside it and setting the side of the tube parallel with the line of the plummet (Fig. 131).

Prepare a small vessel, about 4 ml. in capacity, by drawing out a piece of glass tube at one end in the blowpipe flame, and grind the edge of the open end perfectly level and smooth. Hold the vessel in a small wooden clamp, and fill it completely with mercury from a funnel with a stop-cock (Fig. 132). Then slide a glass plate along the ground edge of the tube; this will remove the excess of mercury, and will leave the surface of the metal exactly level. Now pour the mercury from the vessel into the graduated tube. Remove the air bubbles, which adhere to the inside of the tube, by means of a thin piece of lance-wood, and then read the level



FIGS. 131, 132. MERCURY CALIBRATION OF MEASURING-TUBE.

of the highest point of the meniscus of the mercury by means of the graduations.

Fill the vessel repeatedly in the same way, emptying it each time into the graduated tube, and carefully read the level of the mercury after each addition, preferably by means of a cathetometer (see below) placed at some distance from the tube.

If the cathetometer is not employed, great care must be taken that the eye is at the same level as the mercury surface. This may be ensured by holding behind the tube a small vertical mirror, in which the reflection of the eye is seen behind that of the meniscus. The reflection in the mirror of the highest point of the meniscus must be seen at the centre of the pupil of the eye during the reading.

The weight of the mercury which fills the small vessel is accurately determined, and the temperature of the air is noted. The capacity of the tube between the successive readings may then be found in millilitres from the following expression :

$$v = \frac{g \times (1 \times 0.000182t)}{13.596},$$

in which (*g*) represents the weight of the mercury in grammes, and (*t*) the temperature in °C. at which the calibration is made; while 0.000182 is the coefficient of expansion of mercury and 13.596 is its specific gravity.

The method of calculating the capacity of the tube at each graduation will be understood by reference to p. 112; but the "error of meniscus" must be added to each volume thus obtained, if the tube is to be used for measuring a gas over mercury. The capacities do not however require a meniscus correction if the gas is measured over water, for a reason which is explained below.

The Cathetometer consists of a horizontal telescope sliding on a vertical stem. The telescope is set in a horizontal position by means of a spirit-level and is focussed on the tube; it is then moved vertically on the stem, by turning a screw adjustment, until the point of intersection of the cross-wires exactly corresponds with the highest point of the mercury meniscus, and the graduation is read off. Since the telescope is always horizontal, errors of parallax are avoided.

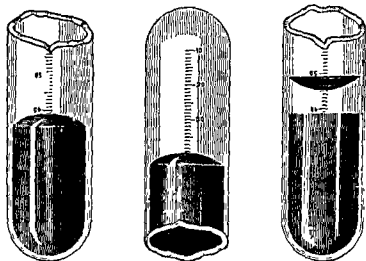


FIG. 183. FIG. 184. FIG. 185.

ERROR DUE TO MENISCUS.

The error due to meniscus is the difference between the reading of the convex surface of the mercury and the reading when the level of the mercury surface is read. This error is shown in the diagrams. In Fig. 183, the reading of the convex surface is 10.0, and the reading when the level of the mercury surface is read is 9.5. In Fig. 184, the reading of the concave surface is 10.0, and the reading when the level of the mercury surface is read is 10.5. In Fig. 185, the reading of the convex surface is 10.0, and the reading when the level of the mercury surface is read is 9.5.

in the inverted tube (Fig. 133), and then introducing a few drops of mercuric chloride solution and again reading the level of the mercury surface. The solution overcomes the repulsive action of the glass on the mercury and

whereas in  
ion.  
division 30  
of the glass  
the volume

between 38.7 and 39.3, that is 0.6, would escape measurement. Hence 0.6 is the Error of Meniscus in this tube.

In practice this error is accordingly equal to double the difference between the reading of the convex surface of the mercury, and the reading when the

surface is levelled by means of mercuric chloride solution. This number must be added to the calculated capacity of the tube when the volume of the gas is read over mercury.

If the tube is to be used for the measurement of a gas over water instead of over mercury, the capacity actually observed in the calibration with mercury should be taken, no correction for the meniscus being made. The convex surface of the mercury during calibration will almost coincide with the concave water-surface when the tube is used in an inverted position, and the "error of meniscus" will therefore be absent.

*Note.* The fouling of the walls of glass tubes by oxidation of the exposed mercury surface may be prevented by just covering the surface with syrupy phosphoric acid (sp. gr. 1.5). This device can, of course, only be used in cases where this acid has no influence on the determination.

*Calibration of the Measuring-tube in the Lunge Nitrometer* (Fig. 141, p. 477). The measuring-tube of the Lunge nitrometer may readily be calibrated by detaching it from the apparatus, stopping up the bottom, and then filling the tube up to the commencement of the graduations with mercury. The tube is clamped vertically. Successive equal volumes of mercury are then added from the small tube, and the readings are taken as has been described on p. 462. The capacity of the tube between successive readings is obtained from the formula given on p. 463. No correction for meniscus is necessary in this case, but if small volumes of gas are to be measured, the top of the tube must be calibrated very accurately.

*Calibration of Measuring-tubes by means of Water.* This method depends on determinations of the capacities of successive portions of the tube by introducing successive known weights of water at a known temperature into the tube; or by allowing them to flow from it. The volume of the water is calculated from its weight, and from this volume the capacity of the tube to each graduation may be determined.

*Calibration of the Hempel Burette* (Fig. 136, p. 466). Since the measurement of the volume of the gas in this burette is made over water, the calibration of the measuring-tube should be made with that liquid and not with mercury.

The method is similar to that used for an ordinary burette (p. 112). Disconnect and clean the measuring-tube and attach a small auxiliary burette to its lower end by means of a glass elbow-tube, which must carry a stop-cock, and stout rubber tubing (Fig. 73, p. 113). The connections inside the rubber tubing should be glass to glass.

Fill the measuring-tube with distilled water, which has been recently boiled and then cooled to the temperature of the room. Run this water through the apparatus until every bubble of air has been removed from round the stop-cocks and from the narrow glass tubes. Then fill the gas burette with the water in such a way that the bottoms of the menisci are on the zero marks of both the gas and the auxiliary burettes. Calibrate the burette by the method described on p. 112, and plot a correction chart (Fig. 74).

As the Hempel burette may be used for the analysis of a small volume of a gas, it is well to calibrate the top part of the measuring-tube by drawing off successive volumes of 1 ml. (nominal) of water into a small, weighed, covered beaker and by determining the weight of each volume of the water.

As the weight of 1 ml. of water at the temperature of the laboratory can be found from the Table on p. 496, this test shows at once if the burette has been graduated recently, and, if necessary, a table of corrections may be compiled or a graph may be drawn.

**Caution.** It should be remembered that in all measurements involving the use of water or of any other liquid which wets glass, it is necessary that a certain time should be allowed for the liquid to drain down the sides of the measuring-tube. The time will vary from half a minute to five minutes, according to the nature of the liquid. For ordinary operations with water an interval of two minutes is ample. The Table on p. 498 giving the permissible times of outflow from burettes may be used here as a guide.

### THE HEMPEL GAS-APPARATUS

This apparatus consists of two parts, the burette, which includes a measuring-tube and a pressure-tube, and the pipette. The gas is usually measured over water or some aqueous solution. A special form of burette must be used when the gas, on account of its solubility, cannot be measured over water (p. 469).

The Hempel Gas-burette (Fig. 136) consists of two connected gas tubes. One of these (a) is not graduated, and is called the *Pressure-tube*. The other (b), known as the *Measuring-tube*, is usually graduated into 100 ml. with 0.2-ml. divisions.

The *Pressure-tube* is expanded at its upper end. The *Measuring-tube* is contracted at the top and terminates in about 2 cm. of thick-walled capillary tube; it may be calibrated as is directed on p. 462.

The lower ends of these two tubes are contracted in diameter, and are bent at right angles. They are fitted into slots in semi-circular, weighted, wooden feet, and are connected with one another by a few feet of narrow rubber tubing.

**The Hempel Gas-pipette.** The Hempel pipette is used as an absorbing vessel in connection with the burette. It is shown in its simplest form in Fig. 137. By submitting a gaseous mixture to the successive action of suitable absorbent reagents in a series of these pipettes, the proportions in which the constituent gases are present in the mixture may be determined.

The simple pipette (Fig. 137) consists of two connected bulbs, (c) and (d), which contain the absorbing liquid. The bulb (c) terminates in a

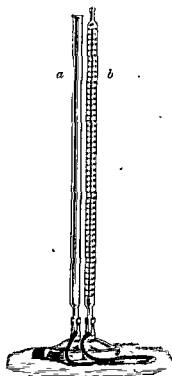
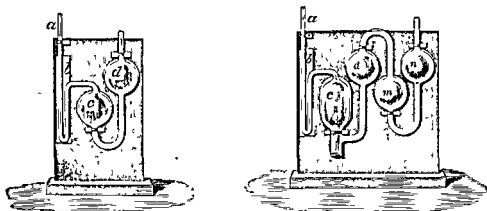


FIG. 136. THE HEMPEL BURETTE.

U-shaped capillary tube (a). Behind this tube is a white porcelain scale (b), which makes the thread of liquid in the capillary visible when the pipette is in use.

A more elaborate absorption pipette is shown in Fig. 138. The bulb (c) is cylindrical in shape, and has an opening at the bottom for the introduction of a solid absorbent, if necessary. This opening is usually closed by a rubber stopper.

Both these forms of the pipette may be fitted with two extra bulbs (m, n), as is shown in Fig. 138. These bulbs are partly filled with water ;



FIGS. 137, 138. HEMPEL GAS-PIPETTES.

they prevent the external air from coming into contact with the absorbent and prevent the escape of vapour from a volatile absorbent.

**Fitting together the Hempel Apparatus.** The burette is connected with the pipette in the manner shown in Fig. 139. Two short thick pieces of rubber tube are slipped over the capillary top of the measuring-tube and on the capillary tube (a) of the pipette. These rubber tubes are bound tightly to the glass with wire, so as to make gas-tight joints. Each piece of rubber tube may carry a spring clip (as shown), but a single clip on the measuring-tube (b) will often be found sufficient.

A piece of thick-walled glass tube, 1 mm. in internal diameter and about 20 cm. in length, is then bent twice at right angles (c. Fig. 139). Each end of this tube is pushed into one of the pieces of rubber tube. Connection can now be made between the absorption-pipette and the measuring-tube by releasing the clips. The measuring-tube and the absorption-pipette can also be disconnected one from the other, without allowing their contents to come into contact with the atmosphere.

**Taking the Sample for Analysis.** Disconnect the pipette (a), leaving the tube (c) and the rubber tubes and clips attached to the measuring-tube (b, Fig. 139). Raise the pressure-tube (d), which has been filled with water, preferably saturated with the gas to be analysed ; then open the clip and pour water into the pressure-tube until the measuring-tube is full and the water begins to flow over from the bent tube (c).

Now close the rubber tube (a) by the clip and squeeze the end of the tube between the finger and thumb, so as to exclude air while it is being connected with the vessel containing the gas to be examined. Then place the pressure-tube (d) at a lower level than the measuring-tube (b), and open the clip again. The gas will thus be drawn over into the measuring-tube ; 50 ml. is a convenient volume.

In order to obtain exactly this volume in the burette, proceed as follows : As soon as rather more than the 50 ml. of gas have entered the measuring-tube, close the rubber tube with the clip. Now close the long rubber tube,

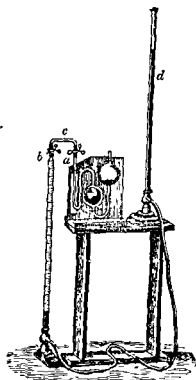


FIG. 139. THE HEMPEL GAS-APPARATUS.

which connects the measuring-tube with the pressure-tube, by pinching it with the fingers. Raise the pressure-tube, and, by relaxing the fingers, allow water to flow into the measuring-tube until it reaches the required graduation. Then at once arrest the inflow of water by pressure of the fingers on the rubber tube. Now open the top of the measuring-tube by relaxing the pressure of the clip for a moment, so as to allow the excess of gas to escape into the air and to leave the remainder at atmospheric pressure. Check the volume of the gas in the measuring-tube after the water has been brought to the same level in both tubes.

The temperature of the room and the barometric pressure need not be read in an ordinary analysis, since these conditions do not vary appreciably during the course of the determination, and measurements of *relative* volumes only are made. But if for any reason the *absolute* volume of the gas is to be found, or its weight is to be determined, the thermometer and barometer must be read to obtain the data necessary for calculating the volume of the gas under normal conditions (p. 461).

**Charging the Pipettes.** Charge each pipette with its special absorbing reagent, filling the bulb (*c*, Fig. 137) completely, but allowing only a small quantity of the liquid to remain in (*d*). The liquid is introduced by pouring it through a funnel into the wide tube above (*d*), and is then drawn nearly to the top of the porcelain scale by applying suction to the capillary tube (*a*). Before a measurement of gas is taken, the liquid should always be brought again to the same level in this capillary tube.

When the pipette is not in use, the reagent should be protected from contact with the air by closing the wide tube with a cork and by capping the capillary tube with a short rubber tube which is stopped with a piece of glass rod.

**Process of Absorption.** After the volume of the gaseous mixture has been noted, absorb its constituent gases successively. Connect the measuring-tube by means of the bent capillary tube with the absorption-pipette containing the first reagent to be used, and squeeze the end of the rubber tube with the fingers when the connection is being made, so as to exclude air. Then raise the pressure-tube and open the clip, so as to drive the gas over from the measuring-tube to the absorption-pipette. As soon as the gas has passed completely into the bulb, close the clip, shake the contents of the bulb gently, and allow the gas to stand in contact

with the absorbent for five minutes. Then transfer the gas to the measuring-tube again by lowering the pressure-tube and opening the clip. As soon as the gas has passed over, close the clip. Raise the pressure-tube until the water in both tubes is at the same level, allow an interval of two minutes for the water to drain from the side of the tube, and read off the volume of the gas. Transfer the gas again to the pipette, and shake it gently with the reagent for one minute; then measure its volume once more in the burette. If the volume is the same as before, the absorption is complete. If a further decrease of volume occurs, the absorption must be repeated a third time, but this is rarely necessary. The volume of the gas remaining in the burette is noted, and another constituent of the gas mixture is absorbed, with a fresh pipette and absorbent.

Subsequent absorptions are effected in a similar way, each gas being absorbed by a suitable reagent (see below). A separate pipette should be kept for each reagent.

The Winkler Burette must be employed for the analysis of gaseous mixtures which contain a constituent soluble in water.

It is of the same shape as the Hempel burette, but the top of the measuring-tube is supplied with a stop-cock, and the bottom with a three-way cock similar to that shown in Fig. 141, p. 477. By this arrangement the measuring-tube can be cut off from the water in the pressure-tube, and a stream of gas can be passed through the stop-cock into the measuring-tube, and thence out into the air by means of the three-way cock.

temperature and pressure are obtained.

Water may then be allowed to flow into the measuring-tube from the pressure-tube in order to absorb the soluble gas, or the measuring-tube may be connected with a Hempel pipette, and further manipulation conducted as with the latter.

### Reagents used for the Absorption of Gases in the Hempel Pipette

**Potassium Hydroxide Solution.** Dissolve 160 grm. of potassium hydroxide in 130 ml. of water: this will give about 200 ml. of solution. The solution is used for absorbing acid gases, *e.g.*, carbon dioxide.

**Alkaline Pyrogallate Solution.** Dissolve 10 grm. of pyrogallie acid in 200 ml. of the above potassium hydroxide solution. The solution should be kept in a pipette of the form shown in Fig. 138, p. 467, and it is used for absorbing oxygen. Departure from these proportions may involve serious error owing to liberation of  $\text{CO}_2$  during the absorption of oxygen.

**Cuprous Chloride Solution.** Pass sulphur dioxide into a solution of 1 part of sodium chloride and 2 parts of crystalline copper sulphate, and wash the precipitate of cuprous chloride by decantation, first with a solution of sulphurous acid, and then with glacial acetic acid. Then press it between filter-paper and dry it in a vacuum desiccator.

During its preparation, storage and use, both this substance and its solution must be excluded from free contact with the air.



The salt is used for absorbing carbon monoxide either in ammoniacal solution (a); or in acid solution (b). The former is generally to be preferred, and must be used when the combustion of hydrogen by palladinised asbestos (p. 472) is to follow the absorption by cuprous chloride.

(a) *The Ammoniacal Solution* is prepared by suspending 15 grm. of cuprous chloride in about 100 ml. of water, contained in a flask of about 250 ml. capacity, and by passing ammonia gas into the liquid until all the cuprous chloride has dissolved and the solution is pale blue in colour. The liquid is then diluted to 200 ml. One millilitre of the solution thus prepared can absorb about 6 ml. of carbon monoxide before it becomes saturated with the gas and useless for further absorption. Absorption of the carbon monoxide is rather slow, and it may be necessary to use further volumes of the reagent if the gas under examination contains more than 10 per cent. of carbon monoxide.

(b) *The Acid Solution* is prepared by dissolving 27 grm. of cuprous chloride in 200 ml. of hydrochloric acid of 1.124 specific gravity. One millilitre of this solution can absorb about 10 ml. of carbon monoxide.

**Ferrous Sulphate**, in cold saturated solution, is used for absorbing nitric oxide.

**Bromine Water**, made by shaking bromine with water until some bromine remains undissolved, is used for absorbing the olefine hydrocarbons.

**Fuming Sulphuric Acid** may be used for absorbing the vapours of benzene and of the olefine hydrocarbons.

### Collection of Gas for Analysis

The Method selected for Collecting a Sample of Gas will vary according to the conditions under which the gas has to be taken, transported and stored. When the gas is collected in the laboratory, it is generally passed direct into the Hempel or Winkler burette; and if a larger quantity has to be stored, it is collected in a glass gas-holder. If the gas must not come into contact with water, it may be passed either into a tube filled with mercury which is closed by inverting its open end in a vessel of mercury, or into a small bell-jar closed with a stop-cock and filled with mercury.

A sample of gas which has to be collected away from the laboratory may occasionally be taken and stored safely as is directed above; or it may be collected by the displacement of air, water, or mercury from a bottle or flask, which is then closed by a tightly-fitting cork, both the upper part of the cork and the neck of the vessel being finally coated uniformly with melted paraffin-wax or

If the supply of gas which is available is small, the tube is prepared as is directed above, and is evacuated and sealed. One of the capillary ends is then cut or broken in the gas to be collected, and it is sealed again after the gas has rushed in to fill the tube.

When the sample is to be transferred to the Hempel burette, a file-mark is made near each end of the sample-tube. One end is then attached by the rubber joint (*a*, Fig. 139, p. 468) to the Hempel burette, while the other end is immersed in a vessel of water or other suitable liquid. Both the ends are then broken off, and the gas is drawn over into the burette in the usual way by lowering the pressure-tube (*d*).

### Determination of Gases by Absorption in the Hempel Apparatus

The volume of each gas is determined from the difference in the volume of the mixture before and after the absorption of that gas. The general procedure and manipulation were described on p. 468, and particulars of the absorbing reagents are on p. 469.

The analysis is made more accurate by previously saturating the water in the burette with the gaseous mixture which is to be analysed. This also applies to the solutions contained in the absorption-pipettes, but, since similar gaseous mixtures are generally analysed by using the same pipettes repeatedly, the liquid in each pipette will gradually become saturated with the gas. However, when a fresh solution is employed, the second and third determinations made with the new solution will, for the above reason, be more accurate than the first, unless a preliminary saturation of the solution with the gas mixture has been effected.

**Carbon Dioxide in Furnace Gases.** Use a simple absorption-pipette containing a solution of potassium hydroxide (p. 469). A more exact method for a small percentage of carbon dioxide in air is described on p. 484.

**Oxygen in Atmospheric Air.** Fill the absorption-pipette with a concentrated solution of alkaline pyrogallate (p. 469).

The average percentage by volume of oxygen in air is 20.96.

**Carbon Dioxide, Oxygen and Nitrogen in a Mixture.** Absorb the gases in the following order in the reagents specified :

1. Carbon dioxide, by potassium hydroxide solution.
2. Oxygen, by alkaline pyrogallate solution.
3. Measure the residual nitrogen.

**Carbon Dioxide, Oxygen, Carbon Monoxide and Nitrogen in a Furnace Gas.** Absorb the gases in the following order by the reagents specified :

1. Carbon dioxide, by potassium hydroxide solution.
2. Oxygen, by alkaline pyrogallate solution.
3. Carbon monoxide, by freshly-prepared cuprous chloride solution (p. 469).
4. Measure the residual nitrogen.

**Carbon Dioxide, Olefines, Benzene, Oxygen, and Carbon Monoxide, Hydrogen and Methane in Coal-gas, Generator-gas and Similar Mixtures.** Absorb the gases in the following order by the reagents specified, using a

Hempel burette containing water saturated with the gas which is to be analysed :

1. Carbon dioxide, by potassium hydroxide solution.
2. Olefines and benzene together, by means of fuming sulphuric acid, subsequently removing the acid fumes by potassium hydroxide solution (*Note*).
3. Oxygen, by alkaline pyrogallate solution.
4. Carbon monoxide, by freshly-made ammoniacal cuprous chloride solution.
5. The residual gas is transferred to a Hempel pipette filled with water, and the hydrogen and methane are determined as is directed on p. 474.
6. Nitrogen will remain as a residue.

*Note.* It is difficult to separate benzene from the olefines. If necessary, benzene may be determined in the presence of ethylene by absorbing both together in fuming sulphuric acid ; the ethylene in another portion of the sample is determined by absorption in bromine water of known concentration, followed by titration of the residual bromine. Although benzene is absorbed by bromine water, the absorption appears to be physical in character, the benzene being neither brominated nor oxidised in the process.

By employing the Winkler Burette (p. 469) or the Lunge Nitrometer (p. 477) the following gases, which are more or less soluble in water, can be determined by means of the absorbents specified in each case :

*Ammonia*, by dilute sulphuric acid.

*Nitric oxide*, by a concentrated solution of ferrous sulphate (*cf.* p. 359).

*Nitrous oxide*, by alcohol.

*Sulphur dioxide, Chlorine, Hydrochloric acid*, by a solution of potassium hydroxide.

*Hydrogen sulphide*, by a solution of copper sulphate, acidified with dilute sulphuric acid.

### Determination of Gases by Absorption in the Hempel Apparatus

**Determination of Hydrogen by Combustion in Air over Palladinised Asbestos.** The hydrogen is mixed with air, and is passed through a glass or fused-silica tube of 1 mm. bore, which contains a gently-heated fibre of asbestos covered with finely-divided palladium (*Note*).

The hydrogen combines with the oxygen of the air to form water, which occupies no appreciable space. The contraction in volume which occurs as a result of the combination is noted, and the volume of hydrogen which was originally present will be equal to two-thirds of this contraction. Hydrogen gas burns readily in this way, carbon monoxide more slowly, and, provided the heating is carefully controlled, methane does not burn at all.

*Note.* A narrow platinum tube containing palladium wire, or a tube of glass or fused silica packed with small pieces of palladium, may replace the tube containing palladinised asbestos.

**Preparation of the Palladinised Asbestos.** Dissolve 1 grm. of palladium in aqua regia, and evaporate the solution to dryness on a water-bath in order to remove free acid. Dissolve the residue in a small quantity of water, add about 5 ml. of a saturated solution of sodium formate, and then add sodium carbonate solution until the reaction of the liquid is strongly alkaline.

Introduce into this liquid about 1 gram. of strong-fibred asbestos, which should absorb the whole of the solution. Remove the asbestos and heat it on the water-bath until it is perfectly dry; then soak the fibres in a little water, place them in a funnel, and wash out the soluble salts.

The palladinised asbestos prepared in this way has a grey colour, and contains about 50 per cent. of palladium. It will cause a mixture of hydrogen and oxygen to combine at the ordinary temperature of the air, but the combination proceeds more rapidly when the fibre is heated.

**Preparation of the Capillary Combustion-tube.** Procure a piece of fused silica or thick-walled, hard-glass tube 1 mm. in bore and 20 cm. in length. Then lay a few loose palladinised asbestos fibres, about 4 cm. in length, side by side on smooth filter-paper, moisten them with a drop or two of water, and twist them into a thread about as thick as stout sewing-cotton. Take up this thread with forceps and push it down the tube, which is meanwhile held vertically. Now fill the tube with water, and bring the asbestos thread into the middle by shaking the tube. Then drain off the water, dry the tube, and bend down its ends at right angles. The tube is now ready to take the place of the ordinary capillary tube (c, Fig. 139, p. 468).

**The Determination of Hydrogen.** It is well to obtain some experience with known volumes of hydrogen and air before undertaking a determination of an unknown volume of hydrogen:

The volume of hydrogen taken should not exceed 25 ml. Read off the volume carefully, then lower the pressure-tube of the burette and allow about 75 ml. of air to enter the measuring-tube. This will supply more than sufficient oxygen to burn all the hydrogen. After adjusting the levels of the water, read the total volume of the gaseous mixture accurately.

Interpose the capillary combustion-tube between the burette and a simple absorption pipette which is filled with water. Next heat the middle of the capillary tube gently over a small flat gas-flame or the flame of a spirit-lamp (the temperature should not exceed  $400^{\circ}\text{C}.$ ), and pass the gaseous mixture very slowly through the tube from the measuring-tube into the pipette by raising the pressure-tube. The end of the asbestos thread will usually glow when the gas reaches it. This "glow" should be reduced to a minimum, because it leads to local heating of the gaseous mixture, and to the oxidation of some methane, if this gas is present. The "glow" may be reduced by reducing the speed of the gas and by removing the flame. If the capillary tube is of glass, care must be exercised, since the removal of the flame may lead to condensation of water and consequent cracking of the tube.

As soon as the gas has passed over completely, draw it back through the heated tube into the measuring-tube. Then in the same way cause the gas to pass forwards and backwards several times over the heated asbestos. In the case of a readily combustible gas like hydrogen, the combustion should now be complete. Read accurately the new volume of the gas, and note if it becomes further reduced after the gas has been passed once more over the hot asbestos. These processes must be repeated until no decrease in volume is noticed after the last passage of the gas over the heated asbestos.

By subtracting the volume of the residual gas from the original volume of the mixture, the contraction of volume which has been caused by the combustion of the hydrogen is found. The volume of hydrogen which has been burnt is equal to two-thirds of this contraction.

**Example.** In a particular determination, the following numbers were obtained:

T ..... 8 ml.  
 II ..... 8.0 ml.  
 ..... 22.8 = 75.2 ml.

[Assuming the percentage volume of oxygen in air to be 21, the volume of oxygen introduced = 15.8 ml. Now 22.8 ml. of hydrogen require 11.4 ml. of oxygen for their complete combustion; hence, even if the gas under analysis were all

the combustion is  
 98.0 - 64.0 = 34 ml.

Hence the volume of hydrogen originally present =  $\frac{34 \times 2}{3} = 22.7$  ml.

### Determination of Hydrogen, Methane and Nitrogen.

In the analysis of coal gas and similar mixtures, the gases mentioned on p. 471 are first removed by absorption.

One of two methods may then be adopted. Either (1) the hydrogen may be first determined by combustion (see above), and the methane may then be mixed with oxygen and exploded; or (2) the hydrogen and methane may be mixed with oxygen and burnt simultaneously. In either case the nitrogen will be measured by difference.

1. *First Method.* The Hempel apparatus is filled with water as usual, and the gas, or an aliquot portion of it, is then mixed with air, and the hydrogen is determined as is described on p. 472. The gaseous mixture will now contain only the methane and nitrogen, together with a known volume of nitrogen and oxygen from the added air. The methane and nitrogen in this mixture are determined as follows:

About 20 ml. of the gas are mixed with more than the volume of oxygen required for their complete combustion, the total volume is then carefully measured and the mixture is fired.

*Note.* Bunsen states that if the proportion of combustible gas in the mixture is less than 20 or more than 64 per cent., oxides of nitrogen may be formed. If

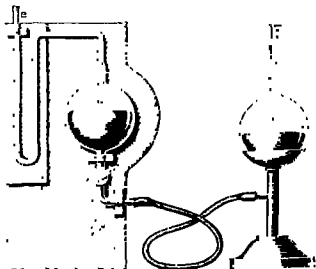
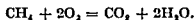


FIG. 140. THE HEMPEL EXPLOSION-PIPETTE.

The mixture is fired by the spark from an induction-coil in a special form of Hempel explosion-pipette (Fig. 140) which contains mercury instead of water.

The gas is introduced into the pipette and is brought approximately to atmospheric pressure. Then the stop-cock (*d*) is closed. To prevent loss of gas during the firing, the rubber tube connecting the burette with the pipette should be bound by wire on to the pipette at (*e*), and closed by inserting a tightly-fitting piece of glass rod. A screen, to protect the face in case of a burst, is placed in front of the pipette and the mixture is sparked.

The decrease in volume caused by the explosion is then measured by opening the stop-cock (*d*) and at once returning the gas to the burette. The further diminution in volume resulting from the absorption of the carbon dioxide produced is also found. The volume of methane originally present in the mixture will be equal to the volume of carbon dioxide absorbed, as is seen from the equation :



The volume of nitrogen in the original mixture is found by subtracting the sum of the volumes of hydrogen and of methane from the volume of the original mixture.

2. *Second Method.* About 30 ml. of the mixture of hydrogen, methane, and nitrogen are made up to 75 ml. by the addition of oxygen (see *Note*, p. 474).

The mixture is fired in the Hempel explosion-pipette as before, the contraction in volume which is caused by the combustion is measured, and the further contraction which results from the absorption of the carbon dioxide by potassium hydroxide solution is also observed. The volumes of hydrogen and of methane are then calculated as follows :

If  $x$  = the contraction in volume caused by firing, and

$y$  = the contraction in volume caused by the subsequent absorption with potash,

$$\text{Then the volume of hydrogen} = \frac{2}{3}(x - 2y)$$

$$\text{and the volume of methane} = y.$$

The above equations are based upon the facts that (1) the contraction of volume caused by firing is due to the combination of free and combined hydrogen with part of the oxygen present, to form water; and (2) the  $\text{CH}_4$  forms its own volume of carbon dioxide.

**Example of Coal-gas Analysis.** The sample of coal-gas was collected in a Hempel burette, which had been filled with water previously saturated with coal-gas. The original volume of gas was 99 ml., and this was treated successively with the following reagents with the results stated below.

1. Potassium hydroxide gave no absorption, hence carbon dioxide was absent.

2. Alkaline pyrogallate solution gave :

Before absorption = 99.0 ml.

After absorption = 98.8 ml.

∴ The volume of oxygen = 0.2 ml. and

The percentage of oxygen =  $0.2 \times \frac{100}{99} = \underline{0.2}$ .

3. Fuming sulphuric acid, followed by potassium hydroxide solution gave

Before absorption = 98.8 ml.

After absorption = 93.5 ml.

∴ The volume of olefines and benzene = 5.3 ml. and

The percentage of olefines and benzene =  $\frac{5.3}{99} \times 100 = \underline{5.4}$ .

4. Cuprous chloride solution gave :

Before absorption = 93.5 ml.

After absorption = 87.0 ml.

∴ The volume of carbon monoxide = 6.5 ml. and

The percentage carbon monoxide =  $6.5 \times \frac{100}{99} = \underline{6.6}$ .

5. The residual 87 ml. of gas, containing methane, hydrogen and nitrogen, were returned to the pipette, and the water in the burette was substituted by water saturated with air.

30.8 ml. of the gas were then mixed with sufficient oxygen in the explosion-pipette, and the total volume was now 75.2 ml. This mixture was fired with a spark from an induction coil, the volume was read off, and the residual gas was then exposed to potassium hydroxide solution. The volumes read were :

Before firing = 75.2 ml.

After firing = 25.9 ml.

∴ The total contraction = 49.3 ml.

Before absorption = 25.9 ml.

After absorption = 13.9 ml.

∴ The carbon dioxide from the methane = 12.0 ml., and

Hence the volume of methane = 12.0 ml., and

The percentage of methane =  $12 \times \frac{87}{30.8} \times \frac{100}{99} = \underline{34.2}$  (Note).

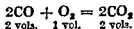
Also the volume of hydrogen =  $\frac{2(49.3 - 2 \times 12)}{3} = \frac{2 \times 25.3}{3} = 16.9$  ml., and

The percentage of hydrogen =  $16.9 \times \frac{87}{30.8} \times \frac{100}{99} = \underline{48.2}$ .

The percentage of nitrogen (by difference) =  $100 - 94.6 = \underline{5.4}$ .

Note. Coal gas may contain a small amount of ethane and of other paraffin hydrocarbons. In this determination such paraffins would count as methane, but this would not have an important influence on the result.

Determination of Carbon Monoxide by Combustion. The methods for determining hydrogen by combustion (pp. 472, 474) also apply to the determination of carbon monoxide in a furnace gas, provided the carbon dioxide present in the mixture has first been removed. From the equation



it will be seen that the original volume of CO is double the contraction caused by its combustion; or to two-thirds of the total contraction caused by the combustion, followed by the absorption of the resulting carbon dioxide by potassium hydroxide solution.

When carbon monoxide is to be determined in the presence of hydrogen, in order to calculate the volume of each of the gases, it is therefore necessary to note both the contraction caused by the firing and the loss of volume which is afterwards caused by the absorption of the resulting carbon dioxide.

### THE LUNGE NITROMETER

The Lunge Nitrometer (Fig. 141) is so called because it was originally devised by Lunge for the analysis of "nitrous vitriol." It can be used in many analytical processes which involve the measurement of a gas.

Like the Hempel burette, it consists of two tubes, the measuring-tube and the pressure-tube. The measuring-tube (*a*) in Fig. 141 has a capacity of 50 ml., and is graduated in tenths of a millilitre; it may be calibrated as described on p. 465. The measuring-tube is connected by thick-walled rubber tubing with the pressure-tube (*b*), which is not graduated. The apparatus is usually filled with mercury. A three-way stop-cock (*d*) is fitted to the top of the measuring-tube (*a*). This cock is also in connection with a cup (*f*), and a strong capillary tube (*e*). In the figure, the stop-cock is shown making communication between the measuring-tube and the cup. When the stop-cock is turned half round, communication is made between the capillary tube and the measuring-tube; but if the stop-cock is turned only one-quarter round, the capillary tube, the measuring-tube and the cup are all cut off from each other.

It will be seen, therefore, that this stop-cock makes it possible to draw a gas into the measuring-tube through the capillary inlet (*e*). The gas can then be exposed to a liquid reagent by pouring the reagent into the cup (*f*), putting the cup into communication with the measuring-tube (*a*), and drawing the liquid into the measuring-tube by lowering the pressure-tube (*b*). The entrance of air into the measuring-tube through the cup is prevented by turning the stop-cock one-quarter round as soon as all the liquid has entered.

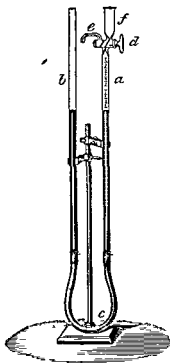


FIG. 141. THE LUNGE NITROMETER.

Another Form of the Nitrometer is used for measuring larger volumes of gas. For this purpose a bulb is blown in the measuring-tube (*a*) immediately before the stop-cock. The bulb has a capacity of nearly 100 ml., the first graduation on the tube below the bulb is for 100 ml.,



and the graduations are continued down the tube to 140 ml. A bulb is also blown in the lower part of the pressure-tube (b) and must be large enough to hold the mercury for the measuring-tube. Some applications of the Lunge nitrometer are described in the following paragraphs.

### Determination of Oxides of Nitrogen in Nitrous Vitriol

Clean and dry the stop-cock (d) of the measuring-tube of the nitrometer (Fig. 141) and the seat into which it fits. Then smear some vaselin lightly over the stop-cock, push it home into its seat, and turn it until the cup (f) is in communication with the measuring-tube (a).

Pour mercury into the pressure-tube until the mercury fills the measuring-tube (a) and just enters the stop-cock, and also rises about 5 cm. above the rubber joint in the glass pressure-tube (b) when the latter is raised. Carefully remove any air bubbles which may be sticking to the inside of the measuring-tube.

Then close the stop-cock, and lower the pressure-tube until the level of the mercury in it is considerably below that of the mercury in the measuring-tube (a). If the apparatus is air-tight and has been freed from air bubbles, no bubble of air will be visible at the top of the mercury column in the measuring-tube (a) after the apparatus has stood for several minutes. Then bring the surfaces of the columns of mercury in both tubes to the same level by raising the pressure-tube (b).

Pour into the cup (f) a known volume of the nitrous vitriol (*Note*), e.g., from 0.5 to 5 ml., according to the quantity of the oxides of nitrogen which the vitriol is believed to contain.

*Note.* If any  $\text{SO}_2$  is present in the nitrous vitriol, it must be oxidised by adding carefully a small quantity of powdered potassium permanganate before the acid is introduced into the nitrometer.

Now open the stop-cock cautiously, and allow the acid, with the exception of a small drop, to run into the measuring-tube (a). Then pour into the cup 3 ml. of concentrated sulphuric acid, free from nitrous compounds, and allow this to run into the measuring-tube (a). Repeat this operation with 3 ml. more of the pure acid, taking care that no air enters the tube. Then stuff the cup (f) with filter-paper to prevent any sulphuric acid left in it from splashing out when the tube is taken.

Grasp the measuring-tube in the hand, unclamp it, and start the evolution of nitric oxide by bringing the acid into contact with the mercury. This is effected by lowering the tube several times almost to the horizontal position, and then by suddenly raising it again to an upright position. Finally shake up the mercury with the acid until no more gas is given off. Use a rotary movement to produce an intimate mixture of the acid with very small globules of mercury.

Then clamp the tubes (a, b) at such relative heights that the gas in the measuring-tube is approximately under atmospheric pressure. For this purpose it may be assumed that 7.6 mm. of the acid in the measuring-tube balance 1 mm. of mercury in the pressure-tube. Allow the apparatus to stand in this position for at least an hour, until its contents have cooled to room temperature.

The levels of the tubes are now once more adjusted, if necessary. A

little concentrated acid is poured into the cup (*f*), and the stop-cock (*d*) is cautiously turned, so as to place the cup and the measuring-tube in communication with one another for a moment. It is easily seen whether the acid in the cup tends to enter the measuring-tube, or to be expelled, and the level of the pressure-tube can be adjusted accordingly, until the gas is exactly under atmospheric pressure.

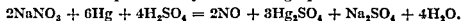
The volume of the gas is then read off, and the atmospheric temperature and pressure are noted down at the same time. It is well to take another reading of the volume after half an hour, and if this agrees with the first, the gas must have attained the atmospheric temperature. As the vapour pressure of the acid is negligible, no correction need be applied to the atmospheric pressure in reducing the volume of the gas to "N.T.P." Each millilitre of nitric oxide at 0° and 760 mm. (p. 461) represents 1.340 milligrams of this gas. This is equivalent to 0.626 milligrams of nitrogen, to 1.698 milligrams of nitrogen trioxide, and to 2.815 milligrams of nitric acid.

After the volume has been read, raise the pressure-tube (*b*); then open the stop-cock, so as to allow both the gas and the acid to pass from the measuring-tube through the capillary tube, the acid being collected in a beaker. Unless the mercury is very dirty, the apparatus may be used again without cleaning. Any nitric or nitrous acid present in the vitriol is reduced to nitric oxide (see equation below).

### Determination of an Alkali Nitrate by the Lunge Nitrometer

This method is similar to that used for the determination of the nitrates in water (p. 358). A quantity of the nitrate, which will evolve rather more than 100 ml. of nitric oxide gas, is weighed, and is introduced into the larger form of nitrometer (p. 477) as is directed below.

The reaction is represented by the following equation :



For practice in the method, weigh out 0.4 gm. of finely-powdered sodium nitrate. Place this powder in the cup (*f*) of the nitrometer, and add about 0.5 ml. of water. As soon as the nitrate has dissolved, draw the solution into the measuring-tube. Then pour about 0.5 ml. of water into the cup, and draw this also into the measuring-tube.

Finally introduce 15 ml. of concentrated sulphuric acid, and proceed as described on p. 478. The apparatus should stand for two hours before the reading of the volume is taken in order that the gas may attain the atmospheric temperature, and another reading, taken half an hour later, should correspond with the first. Each millilitre of gas, at normal temperature and pressure, represents 3.799 milligrams of sodium nitrate.

### Gas Analysis by the Lunge Nitrometer

By employing the Lunge nitrometer with Hempel pipettes, gases which are soluble in water can be determined. Instead of the ordinary Hempel pipettes, similar pipettes of smaller size and partially filled with

mercury may be used. All the gases mentioned on p. 471, except chlorine, can be determined in this way.

In certain cases absorption may be effected in the nitrometer itself. The absorbing liquid is drawn from the cup into a measured volume of the gas, contained in the measuring-tube. The tube is then shaken, and the volume of the residual gas is read off as has already been described.

The Lunge nitrometer may also be used for the analysis of gases dissolved in water or in other liquids. The gases are removed by boiling the water and are received directly in the measuring-tube of the nitrometer. The method is only approximate; more accurate methods, which depend on removing the gases by warming the water under reduced pressure, require special apparatus (see references on p. 519).

*Analysis of Gases dissolved in Water.* Connect a flask, of known capacity, with the capillary tube (e) of the Lunge nitrometer by fitting one end of a short piece of narrow rubber tubing over the capillary tube (e) and attaching the other to a short piece of glass capillary tubing which passes just through a cork in the neck of the flask.

Now fill the nitrometer with mercury and the flask with the liquid containing the gas. Connect the capillary (e) with the measuring-tube (a), and press down the cork into the neck of the flask. The air from the connecting tube is thus transferred to the measuring-tube, and the liquid will fill the capillary tube. Turn the stop-cock, and expel the air from the measuring-tube through the cup (f) by raising the mercury level.

Again connect the flask with the measuring-tube (a), and heat the liquid in the flask until all the dissolved gas has been expelled. Collect the gas in the measuring-tube by lowering the pressure-tube. Allow the gas to cool and measure its volume. Then treat it with suitable absorbents. This method is approximate because a portion of the unboiled liquid containing the gas is necessarily transferred by the boiling to the measuring-tube.

### Determination of Substances which Evolve a Definite Volume of Gas when they are Decomposed

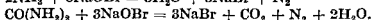
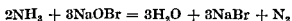
In some cases, the decomposition of the substance may be carried out in the nitrometer itself (e.g., see the determination of alkali nitrate, p. 479), but more often the substance is decomposed in a flask connected to the nitrometer. The material is weighed into a conical flask, a little tube containing the liquid reagent is added (see Fig. 60, p. 69), and the flask is closed with a bung carrying a delivery-tube which is connected to the capillary tube (e) of the nitrometer. When all is ready, the reagent is spilled on to the substance and the gas is evolved. It is usually collected over mercury, but, as the reagent is frequently a dilute, aqueous solution, the gas will nevertheless be wet, and this fact must be remembered when correcting the measured volume of gas to normal temperature and pressure.

*Determination of Ammonium Salts or of Urea by the Nitrometer.* About 0.25 gm. of the solid substance is accurately weighed out, and is introduced into the decomposition-flask; 25 ml. of sodium hypobromite solution (see below) are then introduced into the inner tube. The pressure-tube (b) is

adjusted so that the surface of the mercury in it is about 5 cm. below the stop-cock (*d*), which is then turned so that the measuring-tube (*a*) is connected with the atmosphere. The mercury surfaces in (*a*) and (*b*) are made level and (*a*) is brought into communication with the flask. If the air in the flask is at atmospheric pressure there will be no movement of the mercury. This will not usually be the case, and the mercury levels in (*a*) and (*b*) are again made the same. If, after ten minutes, there is no substantial movement of the mercury, the final adjustment is made and the reading taken. The volume of air now in the tube must be subtracted from the final volume of the gas evolved.

The solution of sodium hypobromite is spilled on to the substance, and the contents of the flask are shaken gently until no more gas is given off. The mercury levels are adjusted approximately, and the whole apparatus is allowed to stand for fifteen minutes. The levels are then adjusted accurately, and the volume of the gas and air in (*a*) and the atmospheric temperature and pressure are read. The volume of gas is then corrected for the vapour pressure of water, and for temperature and pressure.

The reactions which take place are :



The carbon dioxide in the latter case is retained by the sodium hydroxide in the hypobromite solution.

Ammonia evolves, under the above conditions, 97.5 per cent. of its nitrogen, and urea 92 per cent. Each ml. of nitrogen evolved, after correction for temperature, pressure and moisture, accordingly corresponds with 0.001559 gm. of ammonia, and with 0.00291 gm. of urea; or, with 0.00268 gm. of urea, on the assumption that the urea evolves all its nitrogen. This assumption, however, is only correct when much sugar is present (see below).

The *Sodium Hypobromite Solution* is prepared by dissolving 100 gm. of sodium hydroxide in 250 ml. of water, and by mixing 25 ml. of the cold solution with 2.5 ml. of bromine immediately before the reagent is required; this quantity suffices for one determination only.

The Determination of the Percentage of Urea in Urine is frequently required for medical purposes. Thus, 5 ml. of the urine (diluted to 50 per cent. strength if the urea content is unusually high) are placed in the decomposition-flask, and 25 ml. of the sodium hypobromite solution in the inner tube.

The results may be inaccurate because :

(1) Other nitrogenous compounds in the urine besides the urea evolve a small volume of nitrogen, although this amount is usually so small that it may be safely disregarded. (2) The presence of glucose in diabetic urine increases the proportion of nitrogen evolved. The error here may be considerable, but if the diabetic urine is mixed with a weight of cane sugar ten times as great as that of the urea which it contains, the urea will evolve at least 99 per cent. of its nitrogen. (3) Only 92 per cent. of the nitrogen in the urea is evolved (see above). (4) If albumen is present in large amount, it must be coagulated by heating the urine with a few

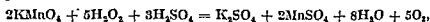
drops of acetic acid : the liquid is then filtered, and the clear filtrate is used for the determination. If this treatment is omitted, the considerable amount of froth produced in the measuring-tube makes the measurement difficult or impossible.

**Determination of Substances which evolve Carbon Dioxide when they are Decomposed.** The same method may also be used for determining the carbon dioxide evolved from carbonates, such as bicarbonates, limestone and bone-charcoal for the evaluation of manganese ores by the determination of oxalates by means of the solubility of carbon dioxide in the low.

It is stated that if 10 ml. of hydrochloric acid of 1.12 specific gravity are used for the decomposition of carbonates, the addition of 7 per cent. to the observed volume gives the correct result. More accurate methods are described on pp. 85-91.

*F. H. C. ... of the Oxygen evolved*

oxide  
1 ml.  
1 the  
red :



from which it is evident that half the volume of oxygen which is liberated is

## MICRO-ANALYSIS OF GASES

The Constant Volume method has recently been adapted by Ambler (p. 519) for micro-purposes, and it enables 1-ml. samples of gas to be analysed with an error of only about 1 per cent. ; or 0.1 per cent. for 15-ml. samples. The method is based on the measurement of the pressure of a gas when it occupies a certain volume at a definite temperature, as distinct from the converse method described in the preceding pages, in which the volume of the gas is measured at a constant pressure and temperature. In addition, rubber connections which may cause leaks or air-locks, are eliminated ; the volume of absorbing solution is reduced so as to minimise its solvent effect, as distinct from its specific chemical absorption for the gas ; and the sensitiveness of the reading devices is increased. Levelling and parallax difficulties are avoided, and only small quantities of mercury and reagent are required. After a little practice the method has proved both simple and rapid, and mixtures of nine constituent gases have been analysed in thirty minutes.

The Apparatus (Fig. 142) consists essentially of three vertically-connected glass bulbs, 1, 3 and 6 ml., respectively, in volume, each or all of which are used according to the volume of sample available. They are enclosed in a constant-temperature water-jacket, and are connected at the base with the manometer  $M_1$ , and at the top, through the 3-way taps  $T_1$  and  $T_2$ , either to the air (at A), to a reservoir ( $R_3$ ), or to a 25-ml. absorption

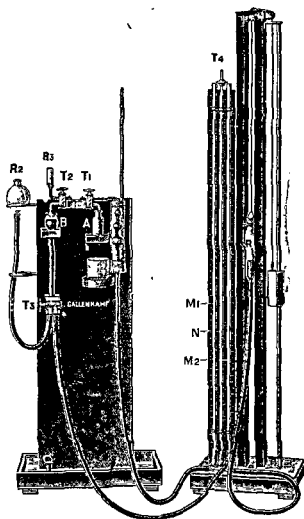


FIG. 142. AMBLER'S APPARATUS FOR THE MICRO-ANALYSIS OF GASES.

bulb B, which in the model illustrated is also provided with explosion electrodes. The connecting tubes are 1-mm. bore glass capillaries. The other tubes shown on the manometer stand are included for convenience.  $M_2$  is an auxiliary manometer which enables the progress of absorption to be followed, and N can be used as a barometer tube.

The manometer reading ( $k$ ) when the bulbs are filled at atmospheric pressure must be known, but need be determined only once, namely, by opening the bulbs to the atmosphere *via*  $T_1$ ,  $T_2$  and  $R_3$  and bringing the mercury in them to the appropriate mark by means of  $R_1$ .

**Procedure.** Fill B with mercury, and transfer the sample to it through A by lowering the reservoir  $R_2$ ; if the sample is contained in an inverted test-tube, a capillary U-tube may be attached to A for this purpose. Manipulate  $T_1$  and  $T_2$  so that the gas is transferred to one or more of the bulbs for measurement, and this is done by taking the manometer reading when the bulb system is filled with gas to the 1-, 3- or 6-ml. mark, as required; during this process the top of the bulbs may be sealed against leaks by allowing mercury from  $R_2$  to fill the horizontal tube between  $T_1$  and the top bulb, *via*  $T_2$  and  $T_1$ .

Now introduce into B, *via* A, the necessary quantity of gas-absorbing solution, transfer the gas from the bulbs to B for absorption (which is aided by shaking this portion of the apparatus *en bloc*), and pass the residue back to the bulbs for measurement, taking care that the sealing column of mercury is at the same point as in the original measurement, and that the temperature of the water-jacket has not changed.

**Calculation.** Let,

$a$  cm. = manometer reading before absorption.

$b$  cm. = manometer reading after absorption.

$k$  cm. = manometer reading with bulbs at atmospheric pressure.

$c$  cm. = barometric pressure.

$w$  cm. = vapour-pressure of water at the temperature of the determination (see p. 499).

$v$  ml. = volume of bulb system used.

Then, the partial pressure of the gas being analysed =  $(a + c - k - w)$ ; this need, of course, be determined only once for each analysis. Then the volume of the gas at normal pressure is, initially,

$$v(a + c - k - w)/76 \text{ ml.}$$

The corresponding volume after absorption is,

$$v(b + c - k - w)/76 \text{ ml.,}$$

so that the volume of gas absorbed is,  $v(a - b)/76$  ml.; or,

$$100(a - b)/(a + c - k - w) \text{ per cent.}$$

## DETERMINATION OF GAS BY ABSORPTION AND TITRATION

### Determination of Carbon Dioxide in Air by Titration, by the Pettenkofer Method

Since carbon dioxide is a product both of respiration and of combustion, it frequently accumulates in the air of closed rooms. A simple and rapid method for its determination in the air is therefore of great importance, because the result enables a judgment to be formed regarding the efficiency of ventilation.

The average percentage by volume of carbon dioxide in the atmosphere is from 0.029 to 0.030.

The Pettenkofer Method of determining Carbon Dioxide in Air depends upon finding the amount of calcium or barium hydroxide which is precipitated as carbonate from solution, when lime- or baryta-water in

excess is shaken with a known volume of the air. A known volume of lime-water, the concentration of which has been determined by titration with a standard solution of an acid, is again titrated with the acid after it has been exposed to a measured volume of the air. The weight and the volume of carbon dioxide, which was present in the known volume of air, can thus be calculated. The following are required :

(a) *A Strong Clear Glass Bottle*, from 8 to 10 litres in capacity, which can be made air-tight by means of an accurately-fitting rubber stopper. The exact capacity of the bottle is ascertained by filling it with water to a scratch on the neck, which marks the bottom of the stopper; the water is then poured into a measuring-vessel in order to determine its volume. The volume of the bottle should be marked permanently on the bottle itself.

The bottle is thoroughly cleaned, rinsed out several times with distilled water and dried, either by leaving it to drain for some time in an inverted position; or, more rapidly, by rinsing it with acetone, draining off as much of the acetone as possible, and by evaporating the remainder by sucking air through the bottle, using a filter-pump. The clean dry rubber stopper is then pushed in, until it reaches the mark on the neck.

(b) *A Hand Bellows* with rubber tube on the nozzle, by means of which the air from any desired locality can be blown into the bottle to displace the air already present in it. They should be clean.

(c) *Saturated Lime-water*, made by repeatedly shaking up freshly-slaked lime with water and a few drops of barium chloride solution in a Winchester quart bottle. The solution is either allowed to stand until it is clear, or it is filtered. The perfectly clear solution is stored in a stoppered Winchester quart bottle.

(d) *A Standard Hydrochloric Acid Solution*, prepared by diluting 50 ml. of N. hydrochloric acid to 1 litre with distilled water, which has been recently boiled for a quarter of an hour (to free it from dissolved carbon dioxide), and then cooled. Each millilitre of this 0.05 N. acid corresponds with 0.566 ml. of carbon dioxide measured at 0° C. and at 760 mm. pressure.

(e) *A Solution of Phenolphthalein* to serve as indicator.

**Procedure.** By means of the bellows (b) a volume of the air which is to be tested, equal to at least six times the volume of the bottle, is blown down to the bottom of the bottle (a); 100 ml. of the lime-water (c) are then at once introduced, the rubber stopper is inserted, and the atmospheric temperature and barometric pressure are noted (*Note 1*).

The bottle is now laid on its side and is rolled along on a level surface, so as to wet the interior with the lime-water. This process is repeated several times during half an hour; 20 ml. of the liquid are then withdrawn from the bottle, by means of a dry pipette with a rubber tube attached to its top, and the bottle is immediately closed (*Note 2*). The 20 ml. are at once titrated in a small flask with the standard hydrochloric acid (d), using phenolphthalein as indicator. The titration should be repeated.

The volume of acid which would be required by 100 ml. of the lime-water, after exposure to the air in the bottle, is calculated from the results obtained. A measured volume of the original lime-water (c) is then



titrated with the standard acid. The difference between the volumes of the acid solution required for 100 ml. of lime-water before and after its exposure to the sample of air is equivalent to the carbon dioxide present.

*Note 1.* A Smaller Bottle of about 2 litres capacity may be used for the air-sample once experience has been obtained in the process. The bottle is closed by a tightly-fitting double-bored rubber stopper, the holes of which are closed by pieces of glass rod. One of these is momentarily removed to allow the introduction of 20 ml. of lime-water, by means of a pipette, into the bottle. After the bottle has been shaken well the lime-water is titrated at once against the standard

being released occasionally by removing the glass rod from the second hole in the stopper.

*Note 2.* It is obviously necessary to guard so far as is possible against the further absorption by the lime-water of carbon dioxide from the open air. Titration in air gives a result which is sufficiently accurate for ordinary purposes, provided it is performed rapidly. The use of the smaller bottle, in which the lime-water is titrated without being removed, is, of course, preferable.

*Example.* The results of an actual determination were as follows:

Capacity of the bottle = 2360 ml.; atmospheric pressure = 762 mm.;  
temperature of the sample of air = 15° C.

20 ml. of the original lime-water required 18.0 ml. of 0.05 N. HCl, 1 ml. of which corresponds with 0.56 ml. of CO<sub>2</sub> at 0° C. and 760 mm. pressure.

20 ml. of the lime-water after being shaken with the sample of air required 15.8 ml. of 0.05 N. HCl.

Therefore the CO<sub>2</sub> in the sample is equivalent to

18.0 - 15.8 = 2.2 ml. of 0.05 N. HCl.

And since each millilitre of this acid corresponds with 0.556 ml. of CO<sub>2</sub>, the volume of CO<sub>2</sub> = 2.2 × 0.556 = 1.22 ml. at 0° C. and 760 mm. pressure.

The volume of air in the bottle at 0° C. and 760 mm. pressure =

$$\frac{2360 \times 762}{760(1 + 0.003665 \times 15)} = 2243 \text{ ml.}$$

Hence the percentage of CO<sub>2</sub> by volume =  $\frac{1.22 \times 100}{2243} = 0.054$ .

## PART VIII

### REFERENCE TABLES, ETC.

ATOMIC WEIGHTS OF ELEMENTS.—See inside front cover.

LOGARITHMS.—See p. 538 and inside back cover.

#### ERRORS AND THEIR STATISTICAL EVALUATION

The variability of the results obtained with many analyses is often a source of anxiety to the operator, although it is inevitable owing in some cases to the nature of the method, and in others to variations in the sample. It is therefore important to be able to assess the true degree of accuracy of the method under the conditions used, and to deduce from this the true value. If a sufficient number of tests is made, this may be done by statistical methods. Other uses of statistical methods are for the selection of the best methods or apparatus for a particular purpose; for the analysis of results obtained in routine tests, as a guide to trends in manufacturing processes; for the estimation of sampling errors; and for the determination of the minimum number of tests necessary to obtain

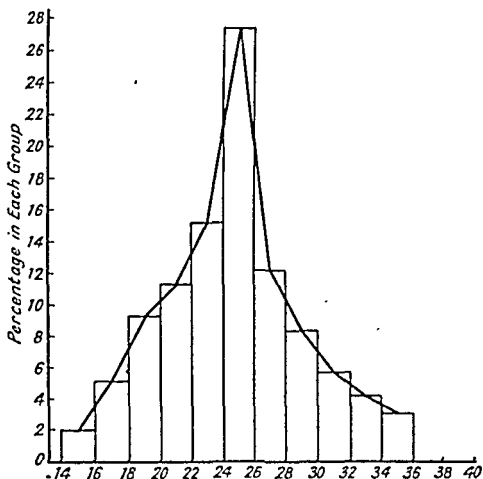


FIG. 143. HISTOGRAM.

a result having a desired degree of accuracy. No attempt can be made to deal with the theory of the subject (see Fisher, p. 518); methods only will be indicated.

**The Histogram, or Frequency Diagram.** When a large number of analyses of one kind are made on a sample, it is extremely unlikely that all the results will be identical; on the other hand, many of them may be coincident with or very near one particular value, and the larger the number of results to which this applies, the more likely is it that this particular value is the correct one. The histogram shows in graphical form how the results are grouped.

Suppose, for the sake of an example, that 1,000 determinations of the hardness of a water have been made, and that the results are distributed as follows:

Hardness (degrees)	14-16	16-18	18-20	20-22	22-24	24-26	26-28	28-30	30-32	32-34	34-36
Number of tests having the value at the head of the column	20	50	90	110	150	270	120	80	55	40	15

The corresponding histogram is plotted in Fig. 143. The horizontal axis corresponds with the 11 groups of values shown in the Table, and the vertical axis with the percentage of results in each group. The histogram shows the frequency of distribution of the observed results around the "central value" ( $V$ ) of 24 to 26. If the histogram is perfectly symmetrical about  $V$  (i.e., if the two halves of the curve fit exactly when the figure is folded along the vertical line representing  $V$ ), then  $V$  will be identical with the mean of all the results, and the curve is termed "normal" to indicate that it expresses Gauss's law of chance. This is not so in Fig. 143; there is a slight bias towards a lower result throughout all the tests. Whether the curve is symmetrical or not, however, the steeper the slope up towards  $V$  from either side the nearer does  $V$  approach the mean value. Obviously by reducing the ranges of the groups used (e.g., to a difference of 0.5 or 1 unit, instead of 2 units, as shown), a smoother curve is obtained.

**Calculation of Means and Errors.** The histogram shows how the results are grouped about the mean value, but it does not give directly the correct result or the probable error of the test. In order to obtain this information the following series of questions are necessary:

from the mean value for the total amount of substance which the sample represents. The greater the standard deviation the more variable are the individual results with respect to the average. The maximum error under the conditions of the analysis represented by the above figures is 3 times the standard deviation, or this quantity above and below the mean value obtained.

accurate mean result to be obtained.

It will be seen that these calculations and that unless (than fifty) they are of limited number of results is small.

## RESULTS OF TYPICAL ANALYSES

The purpose of these tables is to supply information about the compositions of typical specimens of some common materials. This information is given, not so that the student may be able to check his own analyses, but so that he may have data at hand to guide him in his choice of the method to use in the examination of a substance and in his decision as to the weight of the sample to be taken.

Tables I-V are based partly on data supplied through the courtesy of Messrs. The Bureau of Analysed Samples Ltd., Markington, Harrogate, Yorks, and materials of known composition similar to those described in these tables can be obtained from this Bureau.

The Bureau issues two sets of samples—The British Chemical Standards, and Analysed Samples for Students in Metallurgical Analysis. The members of the former group have been analysed each by a number of independent chemists and serve for purposes of reference, for checking methods, and for standardising solutions. The Students' Samples, prepared specially for those who wish to practise quantitative analysis, have been analysed in duplicate by two or three experienced chemists.

The figures given in the tables are only approximate and will be of little value if used as checks. Detailed exact analyses of any of the substances supplied are issued by the Bureau.

TABLE I

*Ferrous Alloys*

	C, (combined)	Si	S	P	Mn	Other Elements
<b>STEEL</b>						
"Pure Iron" . . . . .	0.04	0.03	0.02	0.01	0.04	{ 99.64 Fe 0.03 As 0.05 Cu
Mild Steel . . . . .	0.2	0.1	0.1	0.1	0.7	{ 0.03 As 0.15 Ni 0.01 Cr
Medium Steel . . . . .	0.3	0.2	0.05	0.05	0.5	{ 0.01 Cr
High Carbon Steel . . . . .	0.8	0.2	0.05	0.05	1.0	
Nickel Steel . . . . .	0.3				0.6	4.0 Ni
Chrome-Vanadium Steel . . . . .	0.5	0.2	0.05	0.02	0.5	{ 0.8 Cr 0.3 V 0.4 Ni
Tungsten Steel . . . . .	0.7	0.2	0.07	0.03	0.1	{ 3.0 Cr 0.8 V 4.5 Co 16.0 W
Tungsten-Molybdenum Steel . . . . .	0.7	0.1	0.05	0.02	0.2	{ 0.4 Ni 3.0 Cr 0.8 V 4.0 Co 16.0 W 0.5 Mo
<b>CAST IRON</b>						
Hamatite . . . . .	0.7	2.0	0.05	0.05	0.7	{ 2.4 Graphite 0.05 Ti 0.05 As
Foundry . . . . .	0.8	2.0	0.09	1.0	1.0	{ 2.5 Graphite
High Duty . . . . .	0.9	1.2	0.07	0.3	0.7	{ 1.9 Graphite 2.0 Graphite
Nickel-Chrome . . . . .	0.8	1.6	0.08	0.3	0.9	{ 1.7 Ni 0.5 Cr 0.4 Mo
Austenitic . . . . .		2.0	0.03	0.1	1.0	{ 13.0 Ni 4.0 Cr 5.0 Cu
<b>FERRO ALLOYS</b>						
Ferro-Chromium . . . . .	5.0					70.0 Cr
Low C. Ferro-Chromium . . . . .	0.1					70.0 Cr
Ferro-Tungsten . . . . .						80.0 W
Ferro-Molybdenum . . . . .						72.0 Mo
Ferro-Titanium . . . . .						23.0 Ti
Ferro-Vanadium . . . . .						50.0 V

TABLE II  
Non-ferrous Alloys

	Cu	Zn	Sn	Pb	Fe	Sb	Ni	Al	Mg	Mn	Other Elements
Brass	70.0	27.0	1.0	1.0	0.1						0.05 P
White Metal	87.0	2.0	10.0	0.5	0.1						0.2 P
Phosphor-Bronze	85.0	2.0	10.0	0.5	0.1	0.2					
Germane Bronze	58.0	34.0	2.0	1.0	1.0		1.0	1.5		1.0	
Aluminium Bronze	89.0				0.3			10.0			
Cupro-Nickel	69.0				0.05		30.0		0.03	1.0	0.02 C 0.01 S
Arsenical Copper											0.4 As
Aluminium Silicon					0.3			86.5			13.0 Si
Aluminium Alloy	4.5	2.0	0.05		0.5		2.0	87.0	1.0		
Solder			40.0	60.0							
WHITE METALS											
Lead Base	0.3	0.1	4.5	83.0	0.05	12.0					0.05 As
Tin Base	4.0	0.4	84.0	4.0	0.05	7.5					0.03 Bi

TABLE III  
Minerals (see also Tables IV to VI)

	CaCO <sub>3</sub>	MgCO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Other Compounds
Dolomite	65	33	0.5	0.5	1.0	
Magnesian Limestone	85	10	1.0	1.0	2.0	
Limestone	95	1	1.0	1.0	1.0	
Felspar					65.0	8.0 K <sub>2</sub> O 3.0 Na <sub>2</sub> O 0.05 P
Iron Ore	2.0 CaO	1.0 MgO	58 Fe	2.0	8.0	1.4 CO <sub>2</sub> 0.1 Ti
Chrome Iron Ore		18 MgO	13 Fe			30.0 Cr

TABLE IV  
Sulphide Ores and Concentrates

	S	Fe	Cu	Zn	Pb	As	Mn	Ag	Other Elements
Iron Pyrites . . .	48	40	2					0.2	{ <sup>22</sup> Ni
Burnt Pyrites . . .	3	60	3					0.1	{ <sub>2</sub> Co
Copper Pyrites . . .	30	28	25					0.1	{ 0.1 Sb
Zinc Blende . . .	25		40	47	25			0.1	{ 0.02 Bi
Copper-Lead Matte . . .			17		7	26			
Copper-Nickel Speiss . . .		1.5	0.1	3	75	0.3	0.2		
Lead Concentrates . . .	14							Cd	0.2 CaF
Zinc Concentrates . . .	30	8.0	1	.50	1	0.1	0.3	0.3	{ 2.0 Sn
Tin Concentrates . . .	0.05	1.5	0.01	—	0.5	0.1	0.2	—	{ 0.5 WO <sub>3</sub>

TABLE V  
*Miscellaneous Substances and Fuels*

	CaO	MgO	FeO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	
Basic Slag	45	7	12	4	16	13	3	Water Soluble P <sub>2</sub> O <sub>5</sub> 14
Superphosphate						15		{ Inert SiO <sub>2</sub> 1 SO <sub>3</sub> 1
Portland Cement	65	1	Fe <sub>2</sub> O <sub>3</sub> 4	6	20		Mn 50	Available Oxygen 15 CaF 90
Pyrolusite					6			
Fluor Spar								

	Specific gravity	Volatiles	Coke yield	Coke type	Carbon	Calorific value
Dry, Long Flame, Sand Coal	1.25	45-50	50-58	Powdery	75-80	8,000-8,500
Bituminous Furnace	1.30	33-25	60-74	Fused	82-88	8,700-9,200
Short Flame Anthracite	1.38	16-10	80-88	Sintered	90-94	9,200-9,500



TABLE VI  
Lime, Mortar and Silicates

	CaO	CaCO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>	Insol. Silicious Matter	Soluble SiO <sub>2</sub>	Water	Fine Earthy Matter
Lime { Chalk. Grey-stone. Lias.	92 78 72	3.5 0.7 0.7	1.6 3.5 6.0	0.4 0.8 0.3	10 15.5	2.5 6.8 5.0	3.4 8.5 8.5
Mortar { I. II.* III.	6.4 6.4 9.0	5.9	1.5 1.6 1.1	Coarse Insol. Matter 73.5 57 62.5	2.2 1.4 0.7	Uncombined 2.2 1.6 3.0 Combined 11 15 14	
(Glass { Bohemian Window Flint.	10.3 13.4	PbO 37.3	9.6 1.9 2.0	SiO <sub>2</sub> 71.7 70.7 61.3		K <sub>2</sub> O 12.7 9.4 Na <sub>2</sub> O 2.5 13.2	
Felspar . . .	0.5	MgO 0.4	18.7	65.1		11.8 3.4	

\* This Sample also contained 0.5 per cent. of CaSO<sub>4</sub>.TABLE VII  
Manures

	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Organic Matter	Nitrogen	Alkalies	Silicious Matter	Moisture	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>
Coprolites . . .	58	39	4.4	4	8	4	4
Bone Meal { Raw Steamed	46.5 64	17 40	1.3 8.5	13	1.5 1.5 18	7 8 10	6 9
Guano . . .	10						
Superphosphate . . .	Soluble P <sub>2</sub> O <sub>5</sub> 18 Insoluble P <sub>2</sub> O <sub>5</sub> 6 See Table V.	12		10.5	6.5	15	CaSO 42
Basic Slag . . .							

## Standard Buffer Solutions at 20° C.

(Clark and Lubs)

$P_H$	50 ml. 0.1 M. KH ortho- phthalate + $x$ ml. 0.1 N. HCl.	$P_H$	50 ml. 0.1 M. KH ortho- phthalate + $x$ ml. 0.1 N. NaOH.	$P_H$	50 ml. 0.1 M. KH <sub>2</sub> PO <sub>4</sub> + $x$ ml. 0.1 N. NaOH.	$P_H$	50 ml. 0.1 M. H <sub>3</sub> BO <sub>3</sub> (made up in 1.0 M. KCl) + $x$ ml. 0.1 N. NaOH.
	$x$		$x$		$x$		$x$
2.2	46.70	4.0	0.40	5.8	3.72	7.8	2.61
2.4	39.60	4.2	3.70	6.0	5.70	8.0	3.97
2.6	32.95	4.4	7.50	6.2	8.60	8.2	5.90
2.8	26.42	4.6	12.15	6.4	12.60	8.4	8.50
3.0	20.32	4.8	17.70	6.6	17.80	8.6	12.00
3.2	14.70	5.0	23.85	6.8	23.65	8.8	16.30
3.4	9.90	5.2	29.95	7.0	29.63	9.0	21.30
3.6	5.97	5.4	35.45	7.2	35.00	9.2	26.70
3.8	2.63	5.6	39.85	7.4	39.50	9.4	32.00
		5.8	43.00	7.6	42.80	9.6	36.85
		6.0	45.45	7.8	45.20	9.8	40.80
		6.2	47.00	8.0	46.80	10.0	43.90

To obtain the required  $P_H$ , mix the solutions in the proportions indicated, and dilute to 100 ml.

Indicators for the Colorimetric Determination of  $P_H$  Values

(Clark and Lubs, and Cohen)

Indicators	$P_H$ Range	Colour Change	
		Acid	Alkaline
Thymol blue (acid range)	1.2-2.8	rose	yellow
Bromo phenol blue	3.0-4.6	yellow	purple
Bromo cresol green	3.6-5.2	yellow	blue
Bromo cresol purple	5.2-6.8	yellow	purple
Bromo thymol blue	6.0-7.6	yellow	blue
Phenol red	6.8-8.4	yellow	red
Cresol red	7.2-8.8	yellow	purple
Thymol blue (alkaline range)	8.0-9.6	yellow	blue
Phenolphthalein	8.2-10.0	colourless	red

Un  
thym  
lein,  
of so  
with the resulting colours (in spectral order): red-orange, 3; yellow-orange, 5;  
yellow, 6.5; green, 8; green-blue, 9; violet, 11; red-violet, 12.

Density, Specific Volume, and Expansion of Water  
(Chappuis)

Centi- grade Tem- perature.	Volume in ml. of 1 gram of water. (Volume at 4° = 1.)	Density. (Density at 4° = 1.)	Centi- grade Tem- perature	Volume in ml. of 1 gram of water. (Volume at 4° = 1)	Density (Density at 4° = 1)
0	1.00013	0.999868	16	1.00103	0.998971
1	1.00007	0.999927	17	1.00120	0.998803
2	1.00003	0.999968	18	1.00138	0.998624
3	1.00001	0.999992	19	1.00157	0.998435
4	1.00000	1.000000	20	1.00177	0.998234
5	1.00001	0.999992	21	1.00198	0.998023
6	1.00003	0.999968	22	1.00220	0.997802
7	1.00007	0.999933	23	1.00244	0.997570
8	1.00012	0.999876	24	1.00269	0.997329
9	1.00019	0.999809	25	1.00293	0.997077
10	1.00027	0.999728	26	1.00320	0.996816
11	1.00037	0.999633	27	1.00347	0.996545
12	1.00048	0.999525	28	1.00375	0.996265
13	1.00060	0.999404	29	1.00404	0.995976
14	1.00073	0.999271	30	1.00434	0.995678
15	1.00087	0.999127	31	1.00475	0.995371

## Calibration of Volumetric Apparatus

If a litre flask has been graduated correctly at 20° C., this table shows in grammes how much less than 1,000 grammes is the weight of the counterpoise required to balance that quantity of water which will exactly fill the flask to the mark at different temperatures. When carrying out the calculations, the following assumptions were made :

Counterpoising weights of brass, of density 8.5.

Coefficient of cubical expansion of glass = 0.000027 per degree C.

Air temperature the same as that of the water, and the air half-saturated with water vapour.

Barometric pressure = 760 mm.

T°C	00	01	02	03	04	05	06	07	08	09
10	1.64	1.65	1.65	1.66	1.67	1.67	1.68	1.69	1.69	1.70
11	1.70	1.71	1.72	1.73	1.74	1.74	1.75	1.76	1.76	1.77
12	1.78	1.79	1.80	1.81	1.82	1.82	1.83	1.84	1.85	1.86
13	1.87	1.88	1.89	1.90	1.91	1.92	1.93	1.94	1.95	1.96
14	1.97	1.98	1.99	2.00	2.02	2.03	2.04	2.05	2.06	2.08
15	2.09	2.10	2.11	2.12	2.14	2.15	2.16	2.17	2.19	2.20
16	2.21	2.22	2.23	2.25	2.26	2.28	2.29	2.30	2.32	2.33
17	2.35	2.36	2.38	2.39	2.41	2.42	2.44	2.45	2.47	2.48
18	2.50	2.51	2.53	2.54	2.56	2.58	2.60	2.61	2.62	2.64
19	2.65	2.66	2.68	2.70	2.72	2.74	2.76	2.77	2.78	2.80
20	2.82	2.83	2.85	2.87	2.89	2.91	2.93	2.95	2.97	2.98
21	3.00	3.02	3.04	3.06	3.08	3.10	3.12	3.14	3.16	3.17
22	3.19	3.21	3.23	3.25	3.27	3.29	3.31	3.33	3.35	3.37
23	3.40	3.42	3.44	3.46	3.48	3.50	3.52	3.55	3.57	3.59
24	3.61	3.63	3.65	3.67	3.70	3.72	3.74	3.77	3.79	3.81
25	3.83	3.86	3.88	3.90	3.92	3.95	3.97	4.00	4.02	4.04
26	4.06	4.08	4.11	4.13	4.15	4.18	4.20	4.23	4.25	4.28
27	4.30	4.32	4.35	4.37	4.40	4.43	4.45	4.48	4.50	4.53
28	4.55	4.57	4.60	4.62	4.65	4.68	4.70	4.73	4.75	4.78
29	4.81	4.83	4.86	4.89	4.91	4.94	4.96	4.99	5.02	5.05
30	5.07	5.09	5.12	5.15	5.18	5.21	5.23	5.26	5.29	5.32

Further small corrections for pressure and air temperature can be made as follows :—

For pressure. To the appropriate figure in the Table add

$$0.0014 \times (\text{barometer reading} - 760) \text{ grammes.}$$

For temperature. Add

$$0.004 \times (20 - \text{air temperature in } ^\circ\text{C.}) \text{ grammes}$$

*Example.*

Temperature of water in vessel = 17.4° C.

Barometer = 750 mm.

Air temperature = 13° C.

Then weight of counterpoise required to balance the water which will exactly fill a correctly-calibrated litre flask to the mark is :

$$1000 - [2.41 + 0.0014 (750 - 760) + 0.004 (20 - 13)] \text{ gm.} \\ = 1000 - (2.41 - 0.014 + 0.028) = 997.58 \text{ gm.}$$

### Permissible Times of Outflow for Pipettes and Burettes

(National Physical Laboratory, Class A)

#### NORMAL PIPETTES

Capacity, ml. . . . .	5	10	50	100	250
Time of outflow, secs. . . . .	10-20	15-25	25-40	30-60	50-75

#### PIPETTES GRADUATED ALONG THEIR WHOLE LENGTH

Graduated length, cm. . . . .	15	20	25	30	35
Time of outflow, secs. . . . .	30-60	35-70	40-80	50-100	60-120

#### BURETTES

Graduated length, cm. . . . .	15	20	25	30	35	40	45	50	55	60	65	70
Time of outflow, secs. . . . .	30	40	50	60	70	80	90	100	110	120	130	140
	to	to	to	to	to	to	to	to	to	to	to	to
	60	75	90	105	120	135	150	165	180	195	210	225

*Note 1.* For volumes or lengths not tabulated, the permitted times are those specified for the next largest size.

*Note 2.* For pipettes, the 15 seconds draining-time is allowed in addition to the times given above.

Pressure of Aqueous Vapour for each Tenth of a Degree  
Centigrade from 0° to 30° C.

(From the results of Thiesen and Scheel)

Temp °C	Pressure in mm of Mercury	Temp °C	Pressure in mm of Mercury	Temp. °C	Pressure in mm of Mer- cury	Temp. °C	Pressure in mm of Mer- cury	Temp. °C	Pressure in mm of Mer- cury
00	46	60	70	120	105	180	155	240	223
-1	46	-1	71	1	105	1	156	-1	224
-2	47	-2	71	-2	106	-2	157	-2	225
3	47	-3	71	-3	107	-3	158	-3	227
4	47	-4	72	-4	107	-4	159	-4	228
-5	48	5	72	-5	108	-5	160	-5	230
-6	48	-6	73	6	109	-6	161	-6	231
-7	48	-7	73	7	109	-7	162	-7	232
-8	49	8	74	-8	110	8	163	-8	234
9	49	9	74	-9	111	-9	164	9	235
10	49	70	75	130	112	190	165	250	237
-1	50	-1	75	1	112	1	166	1	238
-2	50	2	76	-2	113	2	167	-2	239
-3	50	-3	76	-3	114	-3	168	-3	241
-4	51	-4	77	-4	115	4	169	-4	242
-5	51	-5	78	-5	115	-5	170	-5	244
-6	51	-6	78	-6	116	-6	171	-6	245
7	52	-7	79	-7	117	-7	172	-7	247
-8	52	-8	79	8	118	8	173	-8	248
9	53	-9	80	9	119	-9	174	9	250
20	53	80	80	140	120	200	175	260	251
-1	53	-1	81	-1	120	-1	176	-1	253
-2	54	-2	81	-2	121	-2	177	-2	254
-3	54	-3	82	-3	121	-3	179	-3	256
-4	55	-4	82	-4	122	-4	180	-4	257
-5	55	-5	83	-5	123	-5	181	5	259
6	55	6	83	-6	124	-6	182	-6	260
-7	56	-7	84	-7	125	7	183	-7	262
-8	56	-8	85	-8	126	8	184	-8	263
-9	56	9	85	-9	127	9	185	-9	265
30	57	90	86	150	128	210	186	270	267
1	57	-1	86	-1	129	-1	188	-1	269
-2	58	2	87	-2	130	-2	189	-2	271
-3	58	-3	87	-3	130	-3	190	-3	272
4	58	-4	88	-4	131	-4	191	-4	274
-5	59	-5	89	-5	132	-5	192	5	275
6	59	-6	89	6	133	-6	193	-6	277
-7	60	-7	90	-7	134	-7	195	-7	279
-8	60	-8	90	-8	135	-8	196	-8	280
-9	61	-9	91	9	135	-9	197	-9	282
40	61	100	92	160	136	220	198	280	283
1	61	-1	92	-1	137	-1	199	-1	285
-2	62	-2	93	-2	138	-2	200	-2	287
-3	62	-3	93	3	139	-3	202	-3	288
-4	63	-4	94	-4	140	-4	203	-4	290
-5	63	-5	95	-5	141	-5	204	-5	292
-6	64	-6	95	-6	142	-6	206	-6	294
-7	64	-7	96	-7	143	-7	207	-7	295
-8	65	-8	97	-8	143	-8	208	-8	297
-9	65	-9	97	-9	144	-9	209	-9	299
50	65	110	98	170	145	230	210	290	300
-1	66	-1	99	-1	146	-1	211	-1	302
-2	66	-2	99	-2	147	-2	212	-2	304
-3	67	-3	100	-3	148	-3	214	-3	306
-4	67	-4	101	-4	149	-4	215	-4	307
5	68	-5	101	-5	150	-5	216	-5	309
-6	68	6	102	-6	151	-6	217	-6	311
-7	69	-7	103	-7	152	-7	219	-7	313
-8	69	-8	103	8	153	-8	220	-8	315
-9	70	-9	104	-9	154	-9	221	-9	316



## ALCOHOL TABLE II

Percentage of Proof Spirit by Volume in Dilute Alcohol of known  
Specific Gravity at 60° F. or 15·6° C. Water = 1.

Sp. Gr. in Air at 60° F./60° F. or 15·6° C./15·6° C.	0·0000	0·0002	0·0004	0·0006	0·0008	Sp. Gr. in Air at 60° F./60° F. or 15·6° C./15·6° C.	0·0000	0·0002	0·0004	0·0006	0·0008
0·999	1·16	0·93	0·70	0·46	0·23	0·973	40·06	39·72	39·38	39·04	38·70
0·998	2·33	2·09	1·86	1·62	1·39	0·972	41·77	41·43	41·09	40·75	40·41
0·997	3·52	3·28	3·04	2·80	2·57	0·971	43·47	43·13	42·79	42·45	42·11
0·996	4·73	4·49	4·24	4·00	3·76	0·970	45·14	44·81	44·48	44·15	43·81
0·995	5·98	5·73	5·48	5·23	4·98	0·969	46·77	46·45	46·13	45·80	45·47
0·994	7·24	6·99	6·74	6·48	6·23	0·968	48·38	48·06	47·74	47·42	47·10
0·993	8·51	8·25	8·00	7·74	7·49	0·967	49·98	49·66	49·34	49·02	48·70
0·992	9·82	9·56	9·29	9·03	8·77	0·966	51·53	51·22	50·91	50·60	50·29
0·991	11·16	10·89	10·62	10·36	10·09	0·965	53·04	52·74	52·44	52·14	51·84
0·990	12·53	12·25	11·98	11·70	11·43	0·964	54·51	54·22	53·93	53·64	53·34
0·989	13·91	13·66	13·37	13·09	12·81	0·963	55·93	55·65	55·37	55·09	54·80
0·988	15·38	15·09	14·81	14·52	14·23	0·962	57·33	57·05	56·77	56·49	56·21
0·987	16·85	16·55	16·26	15·96	15·67	0·961	58·68	58·41	58·14	57·87	57·60
0·986	18·34	18·04	17·74	17·44	17·15	0·960	60·09	59·76	59·49	59·22	58·95
0·985	19·87	19·56	19·25	18·95	18·64	0·959	61·32	61·07	60·81	60·55	60·29
0·984	21·44	21·12	20·80	20·49	20·18	0·958	62·60	62·35	62·10	61·84	61·58
0·983	23·02	22·70	22·38	22·06	21·75	0·957	63·85	63·60	63·35	63·10	62·85
0·982	24·66	24·33	24·00	23·67	23·34	0·956	65·09	64·85	64·60	64·35	64·10
0·981	26·32	25·98	25·65	25·32	24·99	0·955	66·29	66·05	65·81	65·57	65·33
0·980	27·99	27·65	27·31	26·98	26·65	0·954	67·48	67·25	67·02	66·78	66·54
0·979	29·70	29·35	29·01	28·67	28·33	0·953	68·62	68·40	68·17	67·94	67·71
0·978	31·42	31·07	30·72	30·38	30·04	0·952	69·76	69·54	69·31	69·08	68·85
0·977	33·15	32·80	32·45	32·10	31·76	0·951	70·87	70·65	70·43	70·21	69·99
0·976	34·87	34·52	34·17	33·83	33·49	0·950	71·98	71·76	71·54	71·32	71·10
0·975	36·61	36·27	35·92	35·57	35·22	0·949	73·05	72·84	72·63	72·42	72·20
0·974	38·35	38·01	37·66	37·31	36·96	0·948	74·12	73·91	73·70	73·49	73·27



## SULPHURIC ACID

Percentage by Weight of  $\text{H}_2\text{SO}_4$  present in Aqueous Solution of known Specific Gravity at  $15^\circ \text{C.}/4^\circ \text{C.}$  (*in vacuo*)

(Lunge and Isler)

Specific Gravity.	Percentage of $\text{H}_2\text{SO}_4$	Specific Gravity.	Percentage of $\text{H}_2\text{SO}_4$	Specific Gravity.	Percentage of $\text{H}_2\text{SO}_4$
1.005	0.83	1.190	26.04	1.375	47.47
1.010	1.57	1.195	26.68	1.380	48.00
1.015	2.30	1.200	27.32	1.385	48.53
1.020	3.03	1.205	27.95	1.390	49.06
1.025	3.76	1.210	28.58	1.395	49.59
1.030	4.49	1.215	29.21	1.400	50.11
1.035	5.23	1.220	29.84	1.405	50.63
1.040	5.96	1.225	30.48	1.410	51.15
1.045	6.67	1.230	31.11	1.415	51.66
1.050	7.37	1.235	31.70	1.420	52.18
1.055	8.07	1.240	32.28	1.425	52.69
1.060	8.77	1.245	32.86	1.430	53.11
1.065	9.47	1.250	33.43	1.435	53.59
1.070	10.19	1.255	34.00	1.440	54.07
1.075	10.90	1.260	34.57	1.445	54.55
1.080	11.60	1.265	35.14	1.450	55.03
1.085	12.30	1.270	35.71	1.455	55.50
1.090	12.99	1.275	36.29	1.460	55.97
1.095	13.67	1.280	36.87	1.465	56.43
1.100	14.35	1.285	37.45	1.470	56.90
1.105	15.03	1.290	38.03	1.475	57.37
1.110	15.71	1.295	38.61	1.480	57.83
1.115	16.38	1.300	39.19	1.485	58.28
1.120	17.01	1.305	39.77	1.490	58.74
1.125	17.66	1.310	40.35	1.495	59.22
1.130	18.31	1.315	40.93	1.500	59.70
1.135	18.96	1.320	41.50	1.505	60.18
1.140	19.61	1.325	42.08	1.510	60.65
1.145	20.26	1.330	42.66	1.515	61.12
1.150	20.91	1.335	43.20	1.520	61.59
1.155	21.55	1.340	43.74	1.525	62.06
1.160	22.19	1.345	44.28	1.530	62.53
1.165	22.83	1.350	44.82	1.535	63.00
1.170	23.47	1.355	45.35	1.540	63.43
1.175	24.12	1.360	45.88	1.545	63.85
1.180	24.76	1.365	46.41	1.550	64.26
1.185	25.40	1.370	46.94	1.555	64.67

SULPHURIC ACID (*continued*)

Specific Gravity.	Percentage of $H_2SO_4$	Specific Gravity.	Percentage of $H_2SO_4$	Specific Gravity.	Percentage of $H_2SO_4$
1.560	65.08	1.700	77.17	1.823	90.60
1.565	65.49	1.705	77.60	1.824	90.80
1.570	65.90	1.710	78.04	1.825	91.00
1.575	66.30	1.715	78.48	1.826	91.25
1.580	66.71	1.720	78.92	1.827	91.50
1.585	67.13	1.725	79.36	1.828	91.70
1.590	67.59	1.730	79.80	1.829	91.90
1.595	68.05	1.735	80.24	1.830	92.10
1.600	68.51	1.740	80.68	1.831	92.30
1.605	68.97	1.745	81.12	1.832	92.52
1.610	69.43	1.750	81.56	1.833	92.75
1.615	69.89	1.755	82.00	1.834	93.05
1.620	70.32	1.760	82.44	1.835	93.43
1.625	70.74	1.765	82.88	1.836	93.80
1.630	71.16	1.770	83.32	1.837	94.20
1.635	71.57	1.775	83.90	1.838	94.60
1.640	71.99	1.780	84.50	1.839	95.00
1.645	72.40	1.785	85.10	1.840	95.60
1.650	72.82	1.790	85.70	1.8405	95.95
1.655	73.23	1.795	86.30	1.8410	97.00
1.660	73.64	1.800	86.90	1.8415	97.70
1.665	74.07	1.805	87.60	1.8410	98.20
1.670	74.51	1.810	88.30	1.8405	98.70
1.675	74.97	1.815	89.05	1.8400	99.20
1.680	75.42	1.820	90.05	1.8395	99.45
1.685	75.86	1.821	90.20	1.8390	99.70
1.690	76.30	1.822	90.40	1.8385	99.95
1.695	76.73				

## HYDROCHLORIC ACID

Percentage of Weight of HCl present in Aqueous Solution of known  
Specific Gravity at 15° C./4° C.

(Lunge and Marchlewski)

Specific Gravity.	Percentage of Hydrochloric Acid.	Specific Gravity.	Percentage of Hydrochloric Acid.
1.000	0.16	1.105	20.97
1.005	1.15	1.110	21.92
1.010	2.14	1.115	22.86
1.015	3.12	1.120	23.82
1.020	4.13	1.125	24.78
1.025	5.15	1.130	25.75
1.030	6.15	1.135	26.70
1.035	7.15	1.140	27.66
1.040	8.16	1.145	28.61
1.045	9.16	1.150	29.57
1.050	10.17	1.155	30.55
1.055	11.18	1.160	31.52
1.060	12.19	1.165	32.49
1.065	13.19	1.170	33.46
1.070	14.17	1.175	34.42
1.075	15.16	1.180	35.39
1.080	16.15	1.185	36.31
1.085	17.13	1.190	37.23
1.090	18.11	1.195	38.16
1.095	19.06	1.200	39.11
1.100	20.01		

## NITRIC ACID

Percentage by Weight of  $\text{HNO}_3$  present in Aqueous Solution of known Specific Gravity at  $15^\circ \text{C.}/4^\circ \text{C.}$

(Lunge and Rey)

Specific Gravity.	Percentage of $\text{HNO}_3$	Specific Gravity.	Percentage of $\text{HNO}_3$ .	Specific Gravity.	Percentage of $\text{HNO}_3$ .
1.000	0.10	1.175	28.63	1.350	55.79
1.005	1.00	1.180	29.38	1.355	56.66
1.010	1.90	1.185	30.13	1.360	57.57
1.015	2.80	1.190	30.88	1.365	58.48
1.020	3.70	1.195	31.62	1.370	59.39
1.025	4.60	1.200	32.36	1.375	60.30
1.030	5.50	1.205	33.09	1.380	61.27
1.035	6.38	1.210	33.82	1.385	62.24
1.040	7.26	1.215	34.55	1.390	63.23
1.045	8.13	1.220	35.28	1.395	64.25
1.050	8.99	1.225	36.03	1.400	65.30
1.055	9.84	1.230	36.78	1.405	66.40
1.060	10.68	1.235	37.53	1.410	67.50
1.065	11.51	1.240	38.29	1.415	68.63
1.070	12.33	1.245	39.05	1.420	69.80
1.075	13.15	1.250	39.82	1.425	70.98
1.080	13.95	1.255	40.58	1.430	72.17
1.085	14.74	1.260	41.34	1.435	73.39
1.090	15.53	1.265	42.10	1.440	74.68
1.095	16.32	1.270	42.87	1.445	75.98
1.100	17.11	1.275	43.64	1.450	77.28
1.105	17.89	1.280	44.41	1.455	78.60
1.110	18.67	1.285	45.18	1.460	79.98
1.115	19.45	1.290	45.95	1.465	81.42
1.120	20.23	1.295	46.72	1.470	82.90
1.125	21.00	1.300	47.49	1.475	84.45
1.130	21.77	1.305	48.26	1.480	86.05
1.135	22.54	1.310	49.07	1.485	87.70
1.140	23.31	1.315	49.89	1.490	89.60
1.145	24.08	1.320	50.71	1.495	91.60
1.150	24.84	1.325	51.53	1.500	94.09
1.155	25.60	1.330	52.37	1.505	96.39
1.160	26.36	1.335	53.22	1.510	98.10
1.165	27.12	1.340	54.07	1.515	99.07
1.170	27.88	1.345	54.93	1.520	99.67

## SODIUM HYDROXIDE AND AMMONIA

Percentage by Weight of NaOH and  $\text{NH}_3$  in Aqueous Solutions of known Specific Gravity at  $15^\circ \text{C.}/4^\circ \text{C.}$

(Bousfield and Lowry)

(Lunge and Wiernik)

Sodium Hydroxide.		Ammonia.	
Percentage of NaOH.	Specific Gravity.	Percentage of $\text{NH}_3$ .	Specific Gravity.
1	1.011	1	0.996
2	1.022	2	0.991
3	1.033	4	0.983
4	1.044	6	0.975
5	1.056	8	0.967
6	1.067	10	0.960
7	1.078	12	0.952
8	1.089	14	0.945
9	1.100	16	0.939
10	1.111	18	0.932
12	1.133	20	0.925
14	1.155	22	0.919
16	1.178	24	0.913
18	1.200	26	0.907
20	1.222	28	0.901
22	1.244	30	0.895
24	1.266	32	0.889
26	1.288	34	0.884
28	1.309	35	0.882
30	1.331		
32	1.352		
34	1.373		
36	1.393		
38	1.414		
40	1.433		
42	1.453		
44	1.472		
46	1.491		
48	1.510		
50	1.529		

## POTASSIUM HYDROXIDE

Percentage by Weight of KOH in Aqueous Solutions of known  
Specific Gravity at 15° C./4° C.

(Pickering)

Percentage of KOH.	Specific Gravity.	Percentage of KOH.	Specific Gravity.
1	1.008	26	1.249
2	1.018	27	1.259
3	1.027	28	1.270
4	1.036	29	1.280
5	1.045	30	1.291
6	1.054	31	1.301
7	1.064	32	1.312
8	1.073	33	1.322
9	1.082	34	1.333
10	1.092	35	1.344
11	1.101	36	1.355
12	1.111	37	1.366
13	1.120	38	1.377
14	1.130	39	1.388
15	1.140	40	1.399
16	1.149	41	1.410
17	1.159	42	1.422
18	1.169	43	1.433
19	1.179	44	1.444
20	1.188	45	1.456
21	1.198	46	1.467
22	1.208	47	1.479
23	1.218	48	1.491
24	1.229	49	1.503
25	1.239	50	1.514

## CHARACTERISTICS OF OILS,

OILS AND FATS.							
Name. Mainly in order of Iodine values.	Specific gravity.		Melting-point.	Insoluble fatty acids + unaponifiable (Hehner value).	Reichert-Meissl value (RM).	Saponification value. (Koettstorfer value).	Iodine value.
	°.		°.	Per cent.	Millilitres of 0·1 N. KOH.	Milli- grams of KOH.	Per Cent.
<b>DRYING OILS.</b>							
Linseed . . . .	15	0·9315- 0·9345	-20	95·5	—	192-195	171-201
Hemp-seed . . . .	15	0·9255- 0·9280	—	—	—	192·5	148
Walnut, or nut oil . . . .	15	0·9250- 0·9260	—	95·4	—	195	145
Poppy-seed . . . .	15	0·9240- 0·9270	—	95·2	0·0	195	133-143
<b>SEMI-DRYING OILS</b>							
Cotton-seed . . . .	15	0·9220- 0·9250	3-4	95-96	—	193-195	108-110
Kapok . . . .	15	0·9237	—	95·6	—	190-197	95-110
Sesame . . . .	15	0·9230- 0·9237	—	95·7	1·2	189-193	103-108
Rape (Colza) . . . .	15·5	0·9132- 0·9168	—	95·1	0·3	170-179	94-102
Croton . . . .	15	0·9500	—	89·0	12-13·6	210-215	102-104
Castor . . . .	15·5	0·9600- 0·9679	—	—	1·4	183-188	83-86
<b>NON-DRYING OILS.</b>							
Almond . . . .	15	0·9175- 0·9195	—	96·2	—	191	93-97
Arachis . . . .	15	0·9170- 0·9209	0	95·8	—	190-196	83-100
Olive . . . .	15	0·916	—	95	0·3	185-196	79-89
<b>MARINE ANIMAL OILS</b>							
Cod-liver . . . .	15	0·9210- 0·9270	—	95·3	—	171-189	167
Seal . . . .	15	0·9155- 0·9263	—	95·45	0·07-0·22	189-196	127-141
Whale . . . .	15·5	0·9250	—	93·5	0·7-2·04	188	121-136

## FATS AND WAXES (LEWKOWITSCH)

OILS AND FATS.				MIXED FATTY ACIDS.					
Maugené Thermal Test.	Acetyl value.	Acid value.	Unsaponifiable matter.	Specific gravity.		Melting-point.	Neutralisation number.	Iodine value.	
°C.		Milli-grams of KOH.	Per Cent.	°C.		°C.	Milli-grams of KOH	Mixed Acids	Liquid Acids.
110-26	3.98	0.8-8.4	0.42-1.1	15.5	0.9233	17-21	197	179-209.8	190-201
97	—	—	1.08	—	—	18-19	—	141	—
103	—	—	—	—	—	16-18	—	160	167
88	—	0.7-11.0	0.43	100	0.8886	20.5	199	139	150
75-90	7.6-18	0.0	0.73-1.64	15.5	0.9206 0.9219	35-38	202-208	111-115	147-151
95	—	—	—	18	0.9162	29-36	191	108	—
65.5	—	0.23-66	0.95-1.32	—	—	26-32	200.4	110.45	129-136
55-64	14.7	1.4-13.2	0.58-1.0	100	0.8758	16-19	185.0	99-103	121-125
—	19-32	—	0.55	—	—	—	201	111.5	—
46-47	147-150	0.14-14.6	—	15.5	0.9509	13	192.1	87-93	106.9
52.5	—	1.5	—	—	—	13-14	204	93-96.5	101.7
45-51	—	10	0.54-0.94	100	0.8700	27.7-32	201.6	96-103	105-128
41.5-45	10.64	1.9-60	0.46-1.0	100	0.8749	24-27	193	86-90	95.5-103.5
102-113	4-8	1-25	0.54-7.83	—	—	21-25	204-207	130.5-170	—
92	16.5	1.9-40	0.38-1.4	—	—	22-33	193.2	—	—
92	—	0.5-37	0.92-3.72	100	0.8922	27.0	—	131.2	144.7



## CHARACTERISTICS OF OILS,

OILS AND FATS.							
Name.  Mainly in order of Iodine values.	Specific gravity.		Melting-point.	Insoluble fatty acids + unsaponifi- able (Hehner value).	Reichert-Meissl value (R.M.).	Saponification value. (Koeletorfer value).	Iodine value.
	C°.		C°.	Per cent.	Millilitres of 0.1 N. KOH.	Milli- grams of KOH.	Per cent.
<b>TERRESTRIAL ANIMAL OILS.</b>							
Sheep's foot . . .	15	0.9175	—	—	—	194.7	74.2
Horse's foot . . .	15	0.913- 0.927	—	—	—	185.9	73.8-90
Neat's foot . . .	15	0.914- 0.916	—	95.2	1.0	194.3	69.3- 70.4
<b>OTHER OILS.</b>							
Rosin oil (distilled from crude rosin)	15	0.966- 0.990	—	—	—	10-35	40-80
Mineral oil (burning and lubricating oil from petroleum)						0	0-15
<b>VEGETABLE FATS.</b>							
Cotton-seed-stearin .	15	0.9188- 0.9230	29-32	95.9	—	195	90-103
Palm oil . . .	15	0.921- 0.924	27-42.5	94.97	0.5	196-202	51.5
Cacao butter (cocoa butter) . . .	15	0.9500- 0.976	28-33	94.59	0.2-0.8	193.55	32-41
Palm-kernel oil . .	15	0.9520	23-28	87.6- 91.1	5-6	242-260	13-14
Cocoonut oil . . .	40	0.9115	21-24	88.6-90	7-8.4	246-260	8-9.5
Japan wax . . .	15	0.9700- 0.9800	50-54	90.6	—	217- 237.5	4.9-8.5
<b>ANIMAL FATS.</b>							
Lard . . .	15	0.934- 0.938	36-40.5	93-96	0.6	195.4	50-70
Bone . . .	15	0.914- 0.916	21-22	—	—	190.9	46-55.8
Beef tallow . . .	15	0.943- 0.952	45-50	95.5	0.25	193.2- 200	38-46
Mutton tallow . .	15	0.937- 0.953	44-45	95.5	—	192- 195.2	35-46
Butter . . .	15	0.926- 0.940	28-33	86.5- 89.8	21-32	227	26-38

## FATS AND WAXES (continued)

OILS AND FATS				MIXED FATTY ACIDS					
Maunder thermal test.	Acetyl value.	Acid value.	Unsaturation matter.	Specific gravity.		Melting-point.	Neutralization number.	Iodine value.	
°C.		Milli-grams of KOH.	Per cent.	°C.		°C.	Milli-grams of KOH.	Mixed Acids.	Liquid Acids.
49.5	—	—	—	—	—	—	—	—	—
38	13	—	—	—	—	—	—	—	—
47-48.5	22.0	5	—	100	0.8713-0.8749	29.8-30.8	202.9-206.3	61.9-63.3	—
7.2	—	—	—	—	—	—	—	—	—
0.38	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	27-30	—	94	—
—	18	24-200	—	100	0.8701	47-50	205.6	53.3	94.6
—	2.8	1.1-1.88	—	—	—	48-50	190	33-39	—
—	19-8.4	8-36	—	—	—	25-28.5	258-264	12.0	—
—	0.9-12.3	5-50	—	98-99	0.8354	25-27	258-266	8.4-9.3	54
—	27-31.2	7-33	1.1-1.63	98-99	0.8480	56-62	213.7	—	—
24-27.5	2.6	0.54-1.28	0.23	99	0.8445	43-44	201.8	64	92.1
—	11.3	29.6-53.0	0.5-1.8	—	—	30	200	55.7-57.4	—
—	2.7-8.6	3.5-50.0	—	100	0.8698	43-44	197.2	41.3	92.4
—	—	1.7-14.0	—	—	—	40-50	210	34.8	92.7
—	1.9-8.6	0.45-35.39	—	37.75	0.9075	38-40	210-220	28-31	—

## TABLES FOR REFERENCE

## CHARACTERISTICS OF OILS,

## WAXES.

Name Mainly in order of iodine values	Specific gravity.		Melting-point.	Acid value.	Saponification value. (Koehtstorfer value.)	Reichert-Meissl value (H.M.).	Iodine value.
	C°.		C°.	Milli-grams of KOH.	Milli-grams of KOH.	Millilitres of 0.1 N KOH.	Per cent.
<b>LIQUID WAXES.</b>							
Sperm oil . . . . .	15	0.8799. 0.8835 0.8764	—	—	125.2- 132.6 123- 135.9	1.3	81-90
Arctic sperm oil . . . . .	15		—	—		1.4	67-82.1
<b>SOLID WAXES.</b>							
Carnauba wax . . . . .	15	0.990- 0.999	85-86	4-7	79-95	—	13.5
Wool wax, wool grease	17	0.9413- 0.9449	31-35	—	102.4	—	17.1- 28.9
Beeswax . . . . .	15	0.964- 0.970	61.5- 64.4	19-21	90-98	0.34-0.54	79-111
Spermaceti (Cetin) . . . . .	15	0.905- 0.960	42-49	—	123-135	—	—
Insect wax . . . . .	15	0.926- 0.970	80.5-83	—	80.5-93	—	—

## FATS AND WAXES (continued)

WAXES.		MIXED FATTY ACIDS						ALCOHOLS + UNSAPONIFIABLE.		
Maunder Thermal Test.	Acetyl value.	Fatty acids.	Specific gravity.		Melting-point.	Mean molecular weight.	Iodine value.		Melting-point.	Iodine value.
		Per cent	C°.		C°.		Per cent.	Per cent.	C°.	Per cent
51	45.64	60-64	15.5	0.899	13.3	281-294	83.2-85.6	37-41	25.5-25.7	65
41-47	41.64	61-65	—	—	10.3-10.8	—	82.7	31.7-42.6	23.5-26.5	65
—	55.24	—	—	—	—	—	—	55	—	—
—	23.3	59.8	—	—	41.8	327.5	17	43.1-61.8	33.5	26.4-36
—	15.24	—	—	—	—	—	—	52-55	—	—
—	2.63	—	—	—	—	—	—	51.5	—	—
—	—	—	—	—	—	—	—	—	—	—

## HYDROMETER SCALES

The most important technical scales are the Baumé and the Twaddell. To convert the readings to specific gravities use the formulae:

$$\text{Baumé at } 15^{\circ} \text{ C.} \quad \text{S.G.} = \frac{144.3}{144.3 - R}$$

$$\text{Twaddell at } 66^{\circ} \text{ F., or } 15.6^{\circ} \text{ C.} \quad \text{S.G.} = \frac{1000 + 5R}{1000}$$

"R" is the reading of the hydrometer.

The hydrometers read correctly only at the temperatures stated. At other temperatures, small corrections must be applied.

## THERMOMETRIC SCALES

There are three thermometric scales now in use. Of these the Centigrade is by far the most important, and everything possible should be done to encourage its use for scientific purposes.

The scales are convertible as follows :

$$x^{\circ} \text{ Fahrenheit} \equiv \frac{5}{9} (x - 32)^{\circ} \text{ C.}$$

$$x^{\circ} \text{ Réaumur} \equiv \frac{5}{4} x^{\circ} \text{ C.}$$

where  $x$  is the Fahrenheit or Réaumur reading, respectively.

## WEIGHTS AND MEASURES

Various scales of weights and measures are set out below. The metric scale is invariably used for scientific purposes.

It is important that the student has a clear understanding of the various units.

The primary unit of length is the metre. This is the distance between two lines, under standard conditions, engraved on a prototype preserved in the Bureau International des Poids et Mesures, Sèvres, France. The primary unit of weight is the kilogram, the mass of a prototype preserved in the same place.

The approved primary unit of capacity is the litre, and is the volume occupied by 1 kilogram of pure water at  $4^{\circ} \text{ C.}$  under a pressure of 760 mm. The millilitre (ml.), the thousandth part of a litre, is used as the secondary unit of capacity. One millilitre is very nearly, but not absolutely, equal to 1 cubic centimetre (based on the standard metre), and careful measurements show that

$$1 \text{ ml.} = 1.000028 \text{ c.c.}$$

Similarly, 1 cubic decimetre is very slightly smaller than 1 litre.

The Mohr or G.W.A. (gram. weight in air) unit of volume is still occasionally used. It is the volume occupied by a quantity of water at  $17.5^{\circ} \text{ C.}$  having an apparent weight in air (brass weights) of 1 gram.

## UNITS OF LENGTH

### SCIENTIFIC UNITS.

1 Angström unit ( $\text{\AA}$ )	$= 1 \times 10^{-8} \text{ cm.}$
1 millimicron ( $\mu\mu$ )	$= 1 \times 10^{-7} \text{ cm.}$
1 micron ( $\mu$ )	$= 1 \times 10^{-4} \text{ cm.}$
1 millimetre (mm.)	$= 1 \times 10^{-1} \text{ cm.}$
1 centimetre	$= 1 \text{ cm.}$
1 decimetre	$= 10 \text{ cm.}$
1 metre	$= 10^2 \text{ cm.}$
1 kilometre	$= 10^3 \text{ cm.}$

### ENGLISH UNITS.

1 inch	$= 2.5400 \text{ cm.}$
1 foot	$= 12 \text{ inches} = 30.480 \text{ cm.}$
1 yard	$= 3 \text{ feet} = 91.440 \text{ cm.}$
1 chain	$= 22 \text{ yards} = 20.117 \text{ metres.}$
1 furlong	$= 10 \text{ chains} = 201.17 \text{ metres.}$
1 mile	$= 8 \text{ furlongs} = 1609.36 \text{ metres.}$

## UNITS OF CAPACITY

### ENGLISH UNITS

1 gill	$= 142.06 \text{ ml.}$
1 pint	$= 4 \text{ gills} = 568.24 \text{ ml.}$
1 quart	$= 2 \text{ pints} = 1.13649 \text{ litres.}$
1 gallon	$= 4 \text{ quarts} = 4.54596 \text{ litres.}$

### APOTHECARIES' UNITS

1 minim	$= 0.05919 \text{ ml.}$
1 fluid scruple	$= 20 \text{ minims} = 1.1838 \text{ ml.}$
1 fluid drachm (drm.)	$= 3 \text{ scruples} = 3.5515 \text{ ml.}$
1 fluid ounce (oz.)	$= 8 \text{ drachms} = 28.412 \text{ ml.}$
1 pint	$= 20 \text{ ounces} = 568.24 \text{ ml.}$
1 gallon of water at $16.7^{\circ} \text{ C.}$	weighs 70,000 grains.
1 fluid ounce of water at $16.7^{\circ} \text{ C.}$	weighs 437.5 grains.

## UNITS OF WEIGHT

## AVOIRDUPOIS WEIGHTS

1 grain	= 64.799 mg.
1 dram = 27.34 grains	= 1.772 gm.
1 ounce = 16 drams	= 28.350 gm.
1 pound = 16 ounces	= 453.592 gm.
1 stone = 14 pounds	= 6.350 kg.
1 hundredweight = 8 stones	= 50.802 kg.
1 ton avoird. = 20 hundredw.	= 1016.05 kg.
1 short ton (U.S.A.) = 2000 pounds	= $0.9072 \times 10^3$ gm.
1 metric ton (tonne)	= $1 \times 10^6$ gm.

## APOTHECARIES' WEIGHTS

1 grain	= 64.799 mg.
1 scruple = 20 grains	= 1.296 gm.
1 drachm = 3 scruples	= 3.888 gm.
1 ounce = 8 drachms	= 31.103 gm.
1 pound = 12 ounces	= 373.242 gm.

## TROY WEIGHTS

1 grain	= 64.799 mg.
1 pennyweight (dwt.) = 24 grains	= 1.555 gm.
1 ounce = 20 pennyweights	= 31.103 gm.
1 pound = 12 ounces	= 373.242 gm.
1 metric carat	= 2.00 gm.

## COMPARISON OF WEIGHTS

## DATA FOR CONVERSION OF WEIGHTS AND MEASURES

Cubic feet $\times 6.234$	= gallons.
Cubic inches $\times 0.003605$	= gallons.
Grammes $\times 15.432$	= grains.
Pints $\times 568.245$	= cubic centimetres.
Gallons $\times 4.546$	= litres.
Litres $\times 0.22$	= gallons.
Centimetres $\times 0.3937$	= inches.
Inches $\times 2.54$	= centimetres.
Parts per 100,000 $\times 0.7$	= grains per gallon.

## OTHER UNITS

*Force.* The dyne, that force which when acting on a mass of 1 gm. for 1 sec., produces an acceleration of 1 cm. per sec. per sec. In the ft.-lb.-sec. system the unit is the poundal.

(1 pound weight = $4.45 \times 10^5$ dynes).
(1 poundal = 13825.5 dynes).

*Work.* The erg, a force of 1 dyne acting through a distance of 1 cm.

(1 joule =  $10^7$  ergs).

*Power.* Work per unit time, 1 erg per sec.

(1 watt =  $10^7$  ergs per sec. = 1 joule per sec.)

*Heat.* The calorie, the heat required to raise 1 grm. of water through  $1^\circ$  C.

(1 calorie = 4.186 joules).

The British Thermal Unit (B.Th.U.), the heat required to raise 1 lb. of water through  $1^\circ$  F.

(1 B.Th.U. = 252.0 calories = 1054.8 joules).

*Electrical.* Joule, the work expended per sec. by a current of 1 amp. flowing in a resistance of 1 ohm.

(1 watt = 1 joule per sec.).

(1 kilowatt = 1.34 horse-power).

Coulomb, the quantity of electricity transferred in 1 sec. by a current of 1 amp.

(1 Faraday = 96,494 coulombs).

The Faraday is that quantity of electricity which will deposit the equivalent weight (expressed in grammes) of a metal at the cathode, when a solution of a salt of the metal is electrolysed.

### USEFUL MEMORANDA

Weight of 1 ml. of dry hydrogen at  $0^\circ$  C. and 760 mm. = 0.00008988 grm.

Weight of 1 ml. of dry nitrogen at  $0^\circ$  C. and 760 mm. = 0.0012507 grm.

Weight of 1 ml. of dry air at  $0^\circ$  C. and 760 mm. = 0.001293 grm.

1 grm. of hydrogen at  $0^\circ$  C. and 760 mm. occupies 11.126 litres.

1 grm. of air at  $0^\circ$  C. and 760 mm. occupies 0.773 litre.

Specific gravity of hydrogen, air as unit = 0.0695.

Specific gravity of air, hydrogen as unit = 14.39.

Weight of 1 c.c. of mercury at  $0^\circ$  C. = 13.5951 grm.

Weight of 1 ml. of mercury at  $0^\circ$  C. = 13.5955 grm.

Coefficient of expansion for gases =  $\frac{1}{273}$  = 0.003663.

1 litre = 1000.028 c.c.

Average percentage of oxygen in air, by volume = 20.99.

1 gallon of water weighs 10 lb. avoirdupois.

1 cubic foot of water weighs 62.3 lb. avoirdupois.

A 10 per cent. aqueous solution is approximately 2 ounces avoirdupois in 1 pint.

The capacity of a Winchester bottle is approximately  $2\frac{1}{2}$  litres.

1 assay ton (avoir.) = 32.667 grm.

1 assay ton (short) = 29.167 grm.

1 atmosphere =  $1.013 \times 10^6$  dynes per sq. cm.

= 14.7 lb. per sq. inch.

The gas constant (R) =  $8.314 \times 10^7$  ergs. per degree.

= 0.082 litre-atmospheres per degree.

= 1.9864 calories per degree.

The gramme-molecular weight of any gas at N.T.P. contains  $6.061 \times 10^{23}$  molecules (the Avogadro number).

The weight of an atom of unit atomic weight =  $1.6488 \times 10^{-24}$  grm.

The weight of an atom of hydrogen =  $1.6617 \times 10^{-24}$  grm.

Planck's constant (h) =  $6.547 \times 10^{-27}$  erg. sec.

Boltzmann's constant (k) =  $1.372 \times 10^{-16}$  erg. per degree.

The velocity of light =  $2.99796 \times 10^{10}$  cm. sec.

$c$  = 2.7183.

$\log_{10} x = 0.4343 \log_e x$

$\log_e x = 2.3026 \log_{10} x$

## List of Common Bench Reagents

Reagent.	Approximate normality or molarity	Approximate concentration Grm. per litre	Remarks
<b>Acids</b>			
Sulphuric (conc.)	—	10 per cent.	Sp. gr. 1.84.
Sulphuric (dil.)	4N.	200	Sp. gr. 1.14. Take 260 ml. of concentrated acid and dilute to 2½ litres (capacity of Winchester bottle).
Hydrochloric (conc.)	10N.	33 per cent.	Sp. gr. 1.16.
Hydrochloric (dil.)	4N.	150	Sp. gr. 1.07. 1100 ml. of concentrated acid per Winchester bottle.
Nitric (conc.)	11N.	67 per cent.	Sp. gr. 1.42. Constant boiling mixture.
Nitric (dil.)	4N.	250	Sp. gr. 1.15. 800 ml. of concentrated acid per Winchester bottle.
Acetic (glacial)	—	100 per cent.	Sp. gr. 1.05. M.P. 16.7° C.
Acetic (dil.)	4N.	240	570 ml. of glacial acid per Winchester bottle.
Sulphurous	3N.	120	Saturated solution.
<b>Bases</b>			
Sodium hydroxide	4N.	160	Sp. gr. 1.17. 400 grm. of white sticks per Winchester bottle.
Potassium hydroxide	4N.	224	Sp. gr. 1.20.
Ammonia (conc.)	—	33 per cent.	Sp. gr. 0.88.
Ammonium hydroxide (dil.)	4N.	140	Sp. gr. 0.95. 500 ml. of 0.88 ammonia per Winchester bottle.
Sodium carbonate	2N.	106	700 grm. of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ per Winchester bottle.
Ammonium carbonate	2N.	—	200 grm. of commercial carbonate + 100 ml. of 0.88 ammonia per Winchester bottle.
Barium hydroxide	0.4N.	35	Saturated solution.
Calcium hydroxide	0.04N.	1.7	Saturated solution.
<b>Salts, etc</b>			
Ammonium chloride	4M.	214	
Ammonium molybdate	—	—	See p. 79.
Ammonium oxalate	0.25M.	31	35 grm. crystals of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ per litre.
Ammonium phosphate	0.33M.	44	Use $(\text{NH}_4)_2\text{HPO}_4$ .
Ammonium sulphide	—	—	Saturate 1 vol. of 0.88 ammonia with hydrogen sulphide. Then add 2 vols. of ammonia and 5 vols. of water.
Barium chloride	0.5M.	104	122 grm. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per litre.
Bromine water	0.4M.	32	Saturated solution.
Calcium sulphate	0.015M.	2.0	Saturated solution.
Ferric chloride	0.33M.	54	90 grm. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 10 ml. of concentrated HCl. per litre.
Ferrous sulphate	0.5M.	76	140 grm. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + 100 ml. of dilute $\text{H}_2\text{SO}_4$ per litre.
Lead acetate	0.5M.	162	190 grm. of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ per litre.
Magnesia mixture	—	—	See p. 78.
Mercuric chloride	0.1M.	27	
Nessler's solution	—	—	See pp. 246 and 351.



## List of Common Bench Reagents—continued

Reagent.	Approximate normality or molarity	Approximate concentration Grm. per litre.	Remarks.
Potassium chromate .	0.125M.	25	105 grm. of $K_2FeC_2O_6 \cdot 3H_2O$ per litre.
Potassium dichromate .	0.125M.	37	
Potassium ferrocyanide .	0.25M.	92	
Potassium permanganate.	0.2M.	32	
Potassium thiocyanate .	0.5M.	50	
Silver nitrate .	0.1M.	17	
Sodium acetate .	2M.	160	See pp. 118, 143, 191 and Index.
Sodium phosphate .	0.17M.	24	
Stannous chloride .	0.5M.	93	
Indicators . . . . .	—	—	

## List of Books for Reference

## For the Theory of Analysis

Engelder . . . . .	
Farnsworth . . . . .	
Fisher . . . . .	
Kolthoff and Stenger . . . . .	
Rieman and Neuss . . . . .	<i>Quantitative Analysis. A Theoretical Approach.</i>
Smith . . . . .	<i>Analytical Processes. A Physico-Chemical Interpretation.</i>

## For General Analysis

Crookes . . . . .	<i>Select Methods of Chemical Analysis</i>
Presenius . . . . .	
Mellan . . . . .	
Mitchell . . . . .	
Scott . . . . .	
Treadwell and Hall . . . . .	<i>Analysis.</i>

## For Volumetric Analysis

Berry . . . . .	<i>Volumetric Analysis.</i>
Knecht and Hibbert . . . . .	<i>New Reduction Methods in Volumetric Analysis (Uses of Titanous Chloride.)</i>
Kolthoff and Furman . . . . .	<i>Volumetric Analysis. Vol. II.</i>
Stott . . . . .	<i>Volumetric Glassware.</i>
Sutton-Mitchell . . . . .	<i>A Systematic Handbook of Volumetric Analysis, 12th Edition.</i>

## For Special Methods of Analysis

Britton . . . . .	<i>Conductometric Analysis.</i>
Brode . . . . .	<i>Chemical Spectroscopy.</i>
Clark . . . . .	<i>Determination of Hydrogen Ions.</i>
Kolthoff and Furman . . . . .	<i>Potentiometric Titrations.</i>

## For Special Methods of Analysis—continued

Kolthoff and Lingane	. . .	<i>Polarography.</i>
Kolthoff and Rosenblum	. . .	<i>Acid-Base Indicators.</i>
Pichler	. . . . .	<i>Introduction to the Micro-Technique of Inorganic Analysis.</i>
Radley and Grant	. . .	<i>Fluorescence Analysis in Ultra-Violet Light, 3rd Edition.</i>
Roth-Daw	. . . . .	<i>Pregl's Quantitative Organic Microanalysis.</i>
Sand	. . . . .	<i>Electrochemistry and Electrochemical Analysis, 3 Vols.</i>
Smith	. . . . .	<i>Metallurgical Analysis by the Spectrograph.</i>
Snell	. . . . .	<i>Colorimetric Methods of Analysis, 2 Vols.</i>
Yoe	. . . . .	<i>Photometric Chemical Analysis, Vol. II., Nephelometry.</i>

## For Analysis of Minerals, Rocks and Ores

Berger	. . . . .	<i>A Text-book of Assaying.</i>
Hillebrand and Lundell	. . .	<i>Applied Inorganic Analysis.</i>
Low	. . . . .	<i>Technical Methods of Ore Analysis.</i>
Mellor and Thompson	. . .	<i>A Treatise on Quantitative Inorganic Analysis with Special Reference to the Analysis of Clays, Silicates and Related Materials.</i>
Schoeller and Powell	. . .	<i>The Analysis of Minerals and Ores of the Rarer Elements.</i>

## For Analysis of Metals and Alloys

Ibbotson	. . . . .	<i>The Chemical Analysis of Steel-Works Materials.</i>
Ibbotson and Aitchison	. . .	<i>Analysis of Non-Ferrous Alloys.</i>
Naish and Clennell	. . .	<i>Select Methods of Metallurgical Analysis.</i>
Pigott	. . . . .	<i>Chemical Analysis of Ferrous Alloys and Foundry Materials.</i>
Pile and Johnston	. . .	<i>Tested Methods of Metallurgical Analysis (Non-Ferrous).</i>
Smith	. . . . .	<i>The Sampling and Assay of the Precious Metals.</i>

## For Gas Analysis

Sutton-Mitchell	. . . . .	<i>A Systematic Handbook of Volumetric Analysis, 12th Edition.</i>
Hempel	. . . . .	<i>Methods of Gas Analysis.</i>
Dennis and Nichols	. . .	<i>Gas Analysis.</i>
Haldane	. . . . .	<i>Methods of Air Analysis.</i>
Lunge-Ambler	. . . . .	<i>Technical Gas Analysis.</i>

## For Applied Chemical Analysis (Chiefly Organic)

Allen	. . . . .	<i>Allen's Commercial Organic Analysis, 8th Edition.</i>
Grant	. . . . .	<i>Laboratory Handbook of Pulp and Paper Manufacture.</i>
Humus	. . . . .	<i>Fuel Testing: Laboratory Methods in Fuel Technology.</i>
International Society of Leather Trades' Chemists	. . .	<i>Official Methods of Analysis.</i>
Lloyd Hind	. . . . .	<i>Brewing Science and Practice.</i>
Keane-Thorne	. . . . .	<i>Lunge and Keane's Technical Methods of Chemical Analysis.</i>
Thorpe	. . . . .	
Thresh, Beale and Suckling	. . .	
Cox	. . . . .	
Bolton	. . . . .	

## For Applied Chemical Analysis Chiefly Organic—continued

Lewkowitsch . . . . .	<i>Chemical Technology and Analysis of Oils, Fats and Waxes.</i>
Fryer and Weston . . . . .	<i>Technical Handbook of Oils, Fats and Waxes.</i>
Coleman and Arnall. . . . .	<i>Preparation and Analysis of Organic Compounds</i>
Findlay . . . . .	<i>Practical Physical Chemistry.</i>
Murray . . . . .	<i>Standard Tests for Reagents and "C.P." Chemicals.</i>
Mitchell . . . . .	<i>Recent Advances in Analytical Chemistry (Organic). Vol. I.</i>
Institute of Petroleum Technologists . . . . .	<i>Standard Methods for Testing Petroleum and its Products.</i>
Fuel Research Board . . . . .	<i>Methods of Analysis of Coal and Coke.</i>

## Reference Tables

Grant . . . . .	<i>Reference Tables</i> . . . . .	2d Edition.
Kaye and Laby . . . . .	<i>Reference Tables</i> . . . . .	
Seidell . . . . .	<i>Reference Tables</i> . . . . .	Organic Substances.
Atack . . . . .	<i>The Chemists' Year Book.</i>	

## CHEMICAL FACTORS

For use in gravimetric and volumetric analysis.

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 grm. of B.	Log C
Ag	AgBr	$\frac{107.88}{187.80}$	57.44	1.7593
		$\frac{107.88}{143.34}$	75.26	1.8766
	AgI	$\frac{107.88}{234.80}$	45.95	1.6622
	AgNO <sub>3</sub>	$\frac{107.88}{169.89}$	63.50	1.8028
		$\frac{107.88}{36.46}$	295.89	2.4711
	NaCl	$\frac{107.88}{58.45}$	184.56	2.2661
		$\frac{26.97}{459.40}$	5.871	0.7687
Al	Al(C <sub>6</sub> H <sub>5</sub> ON) <sub>3</sub>	$\frac{26.97 \times 2}{101.94}$	52.91	1.7236
	Al <sub>2</sub> O <sub>3</sub>	$\frac{26.97}{121.99}$	22.11	1.3446
	AlPO <sub>4</sub>	$\frac{26.97 \times 2}{948.75}$	5.685	0.7548
	K <sub>2</sub> SO <sub>4</sub> ·Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·24H <sub>2</sub> O	$\frac{101.94}{459.40 \times 2}$	11.09	1.0448
Al <sub>2</sub> O <sub>3</sub>	Al(C <sub>6</sub> H <sub>5</sub> ON) <sub>3</sub>	$\frac{101.94}{121.99 \times 2}$	41.78	1.6210
	AlPO <sub>4</sub>	$\frac{74.91 \times 2}{197.82}$	75.74	1.8793
As	As <sub>2</sub> O <sub>3</sub>	$\frac{74.91 \times 2}{246.00}$	60.91	1.7847
	As <sub>2</sub> S <sub>3</sub>	$\frac{74.91}{126.92 \times 2}$	29.51	1.4700
	I	$\frac{74.91 \times 3}{167.01}$	134.6	2.1289
	KBrO <sub>3</sub>	$\frac{74.91 \times 2}{310.46}$	48.27	1.6837
	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	$\frac{74.91}{158.1 \times 2}$	23.69	1.3746
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$\frac{74.91}{248.2 \times 2}$	15.09	1.1787
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	$\frac{197.82}{246.00}$	80.41	1.9053
	As <sub>2</sub> S <sub>3</sub>	$\frac{197.82}{310.46}$	63.72	1.8043
	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>			

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 gm. of B.	Log C
As <sub>2</sub> O <sub>3</sub> . .	Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub>	$\frac{229.82}{310.46}$	74.03	1.8694
AsO <sub>4</sub> . .	Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub>	$\frac{138.91 \times 2}{310.46}$	89.49	1.9518
B . .	B <sub>2</sub> O <sub>3</sub>	$\frac{10.82 \times 2}{69.64}$	31.07	1.4924
	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O	$\frac{10.82 \times 4}{381.43}$	11.33	1.0542
	NaOH	$\frac{10.82}{40.00}$	27.05	1.4322
B <sub>2</sub> O <sub>3</sub> . .	NaOH	$\frac{69.64}{40.00 \times 2}$	87.05	1.9397
Ba . .	BaCl <sub>2</sub> · 2H <sub>2</sub> O	$\frac{137.36}{244.30}$	56.23	1.7499
	BaSO <sub>4</sub>	$\frac{137.36}{233.42}$	58.85	1.7697
	HCl	$\frac{137.36}{36.46 \times 2}$	188.4	2.2750
	I	$\frac{137.36}{126.92 \times 3}$	36.08	1.5572
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	$\frac{137.36 \times 2}{294.21}$	93.38	1.9702
BaO . .	BaSO <sub>4</sub>	$\frac{153.36}{233.42}$	65.70	1.8176
Bi . .	Bi <sub>2</sub> O <sub>3</sub>	$\frac{209.00 \times 2}{466.0}$	89.65	1.9526
	BiPO <sub>4</sub>	$\frac{209.00}{304.0}$	68.75	1.8373
	KMnO <sub>4</sub>	$\frac{209.00 \times 5}{158.03 \times 3}$	220.4	2.3433
Br . .	AgBr	$\frac{79.92}{187.80}$	42.56	1.6290
	AgNO <sub>3</sub>	$\frac{79.92}{169.89}$	47.04	1.6725
	NaBr	$\frac{79.92}{102.91}$	77.65	1.8902
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$\frac{79.92}{158.1}$	50.54	1.7037
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	$\frac{79.92}{248.2}$	32.12	1.5068
C . .	CO <sub>2</sub>	$\frac{12.01}{44.01}$	27.29	1.4360
	C <sub>10</sub> H <sub>8</sub>	$\frac{12.01 \times 10}{128.16}$	93.71	1.9718
CO <sub>2</sub> . .	Ba(OH) <sub>2</sub>	$\frac{44.01}{171.38}$	25.08	1.4006

## Chemical Factors—continued

A. Sought	B Weighed as, or Equivalent to.	Formula Wt of A Formula Wt of B	C. Weight of A represented by 100 grm. of B	Log C.
CO <sub>2</sub>	CaCO <sub>3</sub>	$\frac{44.01}{100.09}$	43.97	1.6432
	Ca(OH) <sub>2</sub>	$\frac{44.01}{74.10}$	59.39	1.7737
	HCl	$\frac{44.01}{36.46 \times 2}$	60.35	1.7806
	Na <sub>2</sub> CO <sub>3</sub>	$\frac{44.01}{106.00}$	41.52	1.6182
	CO <sub>2</sub>	$\frac{60.01}{44.01}$	136.4	2.1347
C <sub>2</sub> O <sub>4</sub>	CaCO <sub>3</sub>	$\frac{88.02}{100.09}$	87.94	1.9442
	CaC <sub>2</sub> O <sub>4</sub>	$\frac{88.02}{128.10}$	68.71	1.8370
	CaC <sub>2</sub> O <sub>4</sub> , H <sub>2</sub> O	$\frac{88.02}{146.12}$	60.24	1.7799
	CaO	$\frac{88.02}{56.08}$	156.95	2.1958
	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 2H <sub>2</sub> O	$\frac{88.02}{126.07}$	69.82	1.8440
	KHC <sub>2</sub> O <sub>4</sub> , H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 2H <sub>2</sub> O	$\frac{88.02 \times 2}{254.19}$	69.26	1.8405
	KMnO <sub>4</sub>	$\frac{88.02 \times 5}{158.03 \times 2}$	139.2	2.1436
	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	$\frac{88.02}{134.01}$	65.68	1.8174
	CaO	$\frac{40.08}{56.08}$	71.47	1.8541
	CaCO <sub>3</sub>	$\frac{40.08}{100.09}$	40.04	1.6025
Ca	CaC <sub>2</sub> O <sub>4</sub>	$\frac{40.08}{128.10}$	31.29	1.4954
	CaC <sub>2</sub> O <sub>4</sub> , H <sub>2</sub> O	$\frac{40.08}{146.12}$	27.43	1.4382
	CaF <sub>2</sub>	$\frac{40.08}{78.08}$	51.33	1.7104
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$\frac{40.08 \times 3}{310.28}$	38.75	1.5883
	CaSO <sub>4</sub>	$\frac{40.08}{136.14}$	29.44	1.4689
CaO	KMnO <sub>4</sub>	$\frac{40.08 \times 5}{158.03 \times 2}$	63.41	1.8021
	CaCO <sub>3</sub>	$\frac{56.08}{100.09}$	56.03	1.7484
	CaSO <sub>4</sub>	$\frac{56.08}{136.14}$	41.19	1.6147

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt of A Formula Wt of B	C. Weight of A represented by 100 grm. of B.	Log C.
CaO	KMnO <sub>4</sub>	$\frac{56.08 \times 5}{158.03 \times 2}$	88.72	1.9480
Cd	CdI <sub>2</sub>	$\frac{112.41}{366.25}$	30.69	1.4870
	CdS	$\frac{112.41}{144.47}$	77.81	1.8910
	CdSO <sub>4</sub>	$\frac{112.41}{208.47}$	53.92	1.7318
Ce(SO <sub>4</sub> ) <sub>2</sub>	Fe	$\frac{332.25}{65.84}$	505.0	2.7745
	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O	$\frac{332.25}{392.13}$	84.73	1.9280
Cl	Ag	$\frac{35.46}{107.88}$	32.87	1.5168
	AgCl	$\frac{35.46}{143.34}$	24.74	1.3934
	AgNO <sub>3</sub>	$\frac{35.46}{169.89}$	20.87	1.3196
	NH <sub>4</sub> Cl	$\frac{35.46}{53.50}$	66.28	1.8214
	NaCl	$\frac{35.46}{68.46}$	60.66	1.7829
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$\frac{35.46}{158.1}$	22.43	1.3507
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	$\frac{35.46}{248.2}$	14.29	1.1549
ClO <sub>2</sub>	AgCl	$\frac{83.46}{143.34}$	58.23	1.7651
	Fe	$\frac{83.46}{65.84 \times 6}$	24.91	1.3964
	KClO <sub>3</sub>	$\frac{83.46}{122.56}$	68.10	1.8331
ClO <sub>4</sub>	AgCl	$\frac{99.46}{143.34}$	69.39	1.8413
	KClO <sub>4</sub>	$\frac{99.46}{138.56}$	71.78	1.8560
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	$\frac{99.46}{294.21}$	33.82	1.5291
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$\frac{99.46}{158.1 \times 6}$	10.48	1.0205
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	$\frac{99.46}{248.2 \times 6}$	6.677	0.8246
CN	Ag	$\frac{26.02}{107.88}$	24.12	1.3824
	AgCN	$\frac{26.02}{133.90}$	19.43	1.2885

## Chemical Factors—continued

A. Sought.	B Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 grm. of B	Log C.
CN . .	AgNO <sub>3</sub>	$\frac{26.02 \times 2}{169.89}$	30.63	1.4862
Co . .	CoO	$\frac{58.94}{74.94}$	78.65	1.8957
	Co <sub>3</sub> O <sub>4</sub>	$\frac{58.94 \times 3}{240.8}$	73.42	1.8658
Cr . .	BaCrO <sub>4</sub>	$\frac{52.01}{253.37}$	20.53	1.3123
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	$\frac{52.01 \times 2}{294.21}$	35.36	1.5485
	PbCrO <sub>4</sub>	$\frac{52.01}{323.2}$	16.09	1.2065
Cr <sub>2</sub> O <sub>3</sub> . .	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	$\frac{152.02}{294.21}$	51.67	1.7132
	PbCrO <sub>4</sub>	$\frac{152.02}{323.2 \times 2}$	23.52	1.3715
Cu . .	CuO	$\frac{63.57}{79.57}$	79.89	1.9025
	Cu <sub>2</sub> O	$\frac{63.57 \times 2}{143.14}$	88.82	1.9485
	Cu <sub>2</sub> (CNS) <sub>2</sub>	$\frac{63.57 \times 2}{243.30}$	52.26	1.7181
	Cu(C <sub>7</sub> H <sub>4</sub> O <sub>2</sub> N) <sub>2</sub>	$\frac{63.57}{335.82}$	18.93	1.2771
	CuSO <sub>4</sub> · 5H <sub>2</sub> O	$\frac{63.57}{249.71}$	25.46	1.4058
	I	$\frac{63.57}{126.92}$	50.09	1.6997
	KIO <sub>3</sub>	$\frac{63.57 \times 4}{214.02 \times 7}$	16.97	1.2298
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$\frac{63.57}{158.1}$	40.21	1.6043
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	$\frac{63.57}{248.2}$	25.61	1.4085
CuO . .	Cu	$\frac{79.57}{63.57}$	125.2	2.0975
	Cu <sub>2</sub> (CNS) <sub>2</sub>	$\frac{79.57 \times 2}{243.30}$	65.41	1.8156
F . .	CaF <sub>2</sub>	$\frac{19.00 \times 2}{78.08}$	48.67	1.6872
	CaSO <sub>4</sub>	$\frac{19.00 \times 2}{136.14}$	27.91	1.4458
Fe . .	Fe <sub>2</sub> O <sub>3</sub>	$\frac{55.85 \times 2}{159.70}$	69.94	1.8447
	FeSO <sub>4</sub> · 7H <sub>2</sub> O	$\frac{55.85}{278.02}$	20.09	1.3029



## Chemical Factors—continued

A. Sought	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 gm. of B.	Log C.
Fe	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\frac{55.85}{392.14}$	14.24	1.1535
	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	$\frac{55.85 \times 2}{964.42}$	11.58	1.0637
	I	$\frac{55.85}{126.02}$	44.00	1.6434
	$\text{K}_2\text{Cr}_2\text{O}_7$	$\frac{55.85 \times 6}{294.21}$	113.9	2.0564
	$\text{KMnO}_4$	$\frac{55.85 \times 5}{158.03}$	176.7	2.2472
	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{55.85}{158.1}$	35.32	1.5480
	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$\frac{55.85}{248.2}$	22.50	1.3522
	Fe	$\frac{71.85}{55.85}$	128.7	2.1096
	$\text{Fe}_2\text{O}_3$	$\frac{71.85 \times 2}{159.70}$	89.98	1.9541
	$\text{K}_2\text{Cr}_2\text{O}_7$	$\frac{71.85 \times 6}{294.21}$	146.5	2.1659
$\text{Fe}_2\text{O}_3$	$\text{KMnO}_4$	$\frac{71.85 \times 5}{158.03}$	227.3	2.3566
	Fe	$\frac{159.70}{55.85 \times 2}$	143.0	2.1553
	$\text{K}_2\text{Cr}_2\text{O}_7$	$\frac{159.70 \times 3}{294.21}$	162.8	2.2117
	$\text{KMnO}_4$	$\frac{159.70 \times 5}{158.03 \times 2}$	252.6	2.4025
	$\text{H}_2\text{O}$	$\frac{1.008 \times 2}{18.016}$	11.19	1.0488
H	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	$\frac{18.016 \times 2}{244.30}$	14.75	1.1638
$\text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\frac{18.016 \times 5}{249.71}$	36.07	1.5572
	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$\frac{18.016 \times 2}{126.07}$	28.58	1.4561
$\text{H}_2\text{O}_2$	I	$\frac{34.016}{126.02 \times 2}$	13.40	1.1271
	$\text{KMnO}_4$	$\frac{34.016 \times 5}{158.03 \times 2}$	53.81	1.7309
	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{34.016}{158.1 \times 2}$	10.76	1.0310
	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$\frac{34.06}{248.2 \times 2}$	6.853	0.8359
	Ag		33.50	1.5289
HCl				

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 gm. of B.	Log C.
HCl . . .	AgCl	$\frac{36.46}{143.34}$	25.44	1.4055
	AgNO <sub>3</sub>	$\frac{36.46}{169.89}$	21.46	1.3317
	CaCO <sub>3</sub>	$\frac{36.46 \times 2}{100.09}$	72.86	1.8625
	Na	$\frac{36.46}{23.00}$	158.6	2.2004
	Na <sub>2</sub> CO <sub>3</sub>	$\frac{36.46 \times 2}{106.00}$	68.80	1.8376
	NaCl	$\frac{36.46}{58.45}$	62.38	1.7951
	NaOH	$\frac{36.46}{40.00}$	91.15	1.9598
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O	$\frac{36.46 \times 2}{248.2}$	27.76	1.4434
	Na	$\frac{63.02}{23.00}$	274.0	2.4378
	Na <sub>2</sub> CO <sub>3</sub>	$\frac{63.02 \times 2}{106.00}$	118.9	2.0752
HNO <sub>3</sub> . . .	NaOH	$\frac{63.02}{40.00}$	157.5	2.1974
	As <sub>2</sub> O <sub>3</sub>	$\frac{34.08 \times 3}{197.82}$	51.68	1.7133
	I	$\frac{34.08}{126.92 \times 2}$	13.42	1.1277
H <sub>2</sub> S . . .	BaSO <sub>4</sub>	$\frac{98.08}{233.42}$	42.02	1.6234
	Na	$\frac{98.08}{23.00 \times 2}$	213.2	2.3289
	Na <sub>2</sub> CO <sub>3</sub>	$\frac{98.08}{106.00}$	92.52	1.9663
H <sub>2</sub> SO <sub>4</sub> . . .	NaOH	$\frac{98.08}{40.00 \times 2}$	122.6	2.0885
	Ag	$\frac{200.61}{107.88}$	186.0 (or 92.98)	2.2694
	AgNO <sub>3</sub>	$\frac{200.61}{169.89}$	118.1 (or 59.04)	2.0722
Hg . . .	Hg <sub>2</sub> Cl <sub>2</sub>	$\frac{200.61 \times 2}{472.13}$	84.98	1.9293
	HgCl <sub>2</sub>	$\frac{200.61}{271.52}$	73.88	1.8686
	Hg(CNS) <sub>2</sub>	$\frac{200.61}{316.77}$	63.33	1.8016
	HgS	$\frac{200.61}{232.67}$	86.22	1.9356
	I	$\frac{200.61}{126.92}$	158.1	2.1990

## Chemical Factors—continued

A. Bought.	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 grm. of B.	Log C.
Hg	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{200.61}{158.1}$	126.9	2.1034
I	Ag	$\frac{126.92}{107.88}$	117.6	2.0706
	AgI	$\frac{126.92}{234.80}$	54.06	1.7328
	$\text{AgNO}_3$	$\frac{126.92}{169.89}$	74.71	1.8734
	$\text{As}_2\text{O}_3$	$\frac{126.92 \times 4}{197.82}$	256.6	2.4093
	$\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$	$\frac{126.92}{267.50}$	47.45	1.6762
	KI	$\frac{126.92}{166.02}$	76.45	1.8834
	$\text{KIO}_3$	$\frac{126.92 \times 4}{214.02}$	237.2	2.3751
	$\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$	$\frac{126.92 \times 2}{324.93}$	78.12	1.8929
	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{126.92}{158.1}$	80.27	1.9046
	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$\frac{126.92}{248.2}$	51.14	1.7087
K	KCl	$\frac{39.10}{74.55}$	52.44	1.7197
	$\text{KClO}_4$	$\frac{39.10}{138.55}$	28.22	1.4505
	$\text{K}_2\text{PtCl}_6$	$\frac{39.10 \times 2}{486.17}$	16.08	1.2064
	$\text{K}_2\text{SO}_4$	$\frac{39.10 \times 2}{174.25}$	44.87	1.6520
	Pt	$\frac{39.10 \times 2}{195.23}$	40.06	1.6027
KCl	Ag	$\frac{74.55}{107.88}$	69.11	1.8395
	$\text{AgNO}_3$	$\frac{74.55}{169.89}$	43.88	1.6423
	$\text{KClO}_4$	$\frac{74.55}{138.55}$	53.81	1.7309
	$\text{K}_2\text{PtCl}_6$	$\frac{74.55 \times 2}{486.17}$	30.67	1.4867
	Pt	$\frac{74.55 \times 2}{195.23}$	76.39	1.8830
	Fe	$\frac{294.21}{55.84 \times 6}$	87.81	1.9436
$\text{K}_2\text{Cr}_2\text{O}_7$	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\frac{294.21}{392.13 \times 6}$	12.50	1.0969

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C Weight of A represented by 100 grm. of B.	Log C
$K_2Cr_2O_7$	I	$\frac{294.21}{126.92 \times 6}$	38.63	1.5870
	$Na_2S_2O_3$	$\frac{294.21}{158.1 \times 6}$	31.01	1.4915
	$Na_2S_2O_3, 5H_2O$	$\frac{294.21}{248.2 \times 6}$	19.76	1.2957
KCN	$AgNO_3$	$\frac{65.11 \times 2}{169.89}$	76.65	1.8845
KI	Ag	$\frac{166.02}{107.88}$	153.9	2.1872
	AgI	$\frac{166.02}{234.80}$	70.71	1.8495
	$AgNO_3$	$\frac{166.02}{169.89}$	97.72	1.9900
$KIO_3$	$KIO_3$	$\frac{166.02 \times 2}{214.02}$	155.1	2.1907
	KI	$\frac{214.02}{166.02 \times 2}$	64.46	1.8093
	I	$\frac{214.02}{126.92 \times 6}$	28.10	1.4488
	or	or	or	or
	I	$\frac{214.02}{126.92 \times 4}$	42.16	1.6249
	$Na_2S_2O_3$	$\frac{214.02}{158.1 \times 6}$	22.56	1.3533
	$Na_2S_2O_3, 5H_2O$	$\frac{214.02}{248.2 \times 6}$	14.37	1.1575
	$As_2O_3$	$\frac{158.03 \times 4}{197.82 \times 5}$	63.91	1.8056
	Fe	$\frac{158.03}{55.84 \times 5}$	56.60	1.7528
	$FeSO_4, (NH_4)_2SO_4, 6H_2O$	$\frac{158.03}{392.13 \times 5}$	8.060	0.9063
$KMnO_4$	$H_2C_2O_4, 2H_2O$	$\frac{158.03 \times 2}{126.07 \times 5}$	50.14	1.7002
	I	$\frac{158.03}{126.92 \times 5}$	24.90	1.3962
	$Na_2C_2O_4$	$\frac{158.03 \times 2}{134.01 \times 5}$	47.17	1.6737
	$Na_2S_2O_3$	$\frac{158.03}{158.1 \times 5}$	19.99	1.3008
	$Na_2S_2O_3, 5H_2O$	$\frac{158.03}{248.2 \times 5}$	12.73	1.1048
	KCl	$\frac{94.19}{74.55 \times 2}$	63.18	1.8005

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A. Formula Wt. of B.	C. Weight of A represented by 100 grm. of B.	Log C.
K <sub>2</sub> O	KClO <sub>4</sub>	$\frac{94.19}{138.55 \times 2}$	33.90	1.5314
	K <sub>2</sub> SO <sub>4</sub>	$\frac{94.19}{174.25}$	34.06	1.7329
	K <sub>2</sub> PtCl <sub>6</sub>	$\frac{94.19}{486.17}$	19.37	1.2872
	Pt	$\frac{94.19}{195.23}$	48.26	1.6835
		$\frac{24.32}{348.64}$		
Mg	Mg(C <sub>2</sub> H <sub>3</sub> ON) <sub>2</sub> , 2H <sub>2</sub> O	$\frac{24.32 \times 2}{222.60}$	6.976	0.8436
	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	$\frac{24.32 \times 2}{222.60}$	21.84	1.3393
MgO	Mg(C <sub>2</sub> H <sub>3</sub> ON) <sub>2</sub> , 2H <sub>2</sub> O	$\frac{40.32}{348.64}$	11.56	1.0631
	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	$\frac{40.32 \times 2}{222.60}$	36.21	1.5588
Mn	As <sub>2</sub> O <sub>3</sub>	$\frac{54.93 \times 4}{197.82 \times 5}$	22.16	1.3456
	Fe	$\frac{54.93}{55.84 \times 5}$	19.67	1.2939
	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , 6H <sub>2</sub> O	$\frac{54.93}{392.13 \times 5}$	2.802	0.4474
	KMnO <sub>4</sub>	$\frac{54.93}{158.03}$	34.76	1.5411
	Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	$\frac{54.93 \times 2}{283.82}$	38.67	1.5874
MnO <sub>2</sub>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 2H <sub>2</sub> O	$\frac{86.93}{126.07}$	68.95	1.8386
	I	$\frac{86.93}{126.02 \times 2}$	34.25	1.5346
	KMnO <sub>4</sub>	$\frac{86.93 \times 5}{158.03 \times 2}$	137.5	2.1384
		$\frac{95.95}{143.95}$		
Mo	MoO <sub>3</sub>	$\frac{86.93}{158.1 \times 2}$	66.62	1.8236
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$\frac{86.93}{248.2 \times 2}$	27.49	1.4392
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O	$\frac{86.93}{248.2 \times 2}$	17.51	1.2433
		$\frac{14.008}{101.10}$		
N	KNO <sub>3</sub>	$\frac{14.008}{101.10}$	13.86	1.1417
	NH <sub>4</sub> Cl	$\frac{14.008}{53.50}$	26.18	1.4180
	NaNO <sub>2</sub>	$\frac{14.008}{69.01}$	20.30	1.3075
	CO(NH <sub>2</sub> ) <sub>2</sub>	$\frac{14.008 \times 2}{60.06}$	46.65	1.6684
	HCl	$\frac{14.008}{36.46}$	38.41	1.5845
		$\frac{14.008}{36.46}$		

## Chemical Factors—continued

A. Sought	B Weighed as, or Equivalent to	Formula Wt of A Formula Wt of B	C. Weight of A represented by 100 grm. of B	Log C.
N . . .	$\text{H}_2\text{SO}_4$	$\frac{14\ 008 \times 2}{98\ 08}$	28.56	1.4558
	$\text{NaOH}$	$\frac{14\ 008}{40\ 00}$	35.02	1.5443
	Pt	$\frac{14\ 008 \times 2}{195\ 23}$	14.35	1.1568
	$(\text{NH}_4)_2\text{PtCl}_6$	$\frac{14\ 008 \times 2}{444\ 07}$	6.309	0.8000
	$\text{NH}_3$	$\frac{14\ 008}{17.03}$	82.30	1.9154
$\text{NH}_3$ . . .	$\text{HCl}$	$\frac{17\ 03}{36\ 46}$	46.70	1.6693
	$\text{H}_2\text{SO}_4$	$\frac{17\ 03 \times 2}{98\ 08}$	34.73	1.5407
	$\text{NaOH}$	$\frac{17\ 03}{40\ 00}$	42.57	1.6292
	$\text{KNO}_3$	$\frac{17\ 03}{101.10}$	16.84	1.2265
	$\text{NH}_4\text{Cl}$	$\frac{17\ 03}{53.50}$	31.82	1.5027
	$(\text{NH}_4)_2\text{PtCl}_6$	$\frac{17\ 03 \times 2}{444\ 07}$	7.670	0.8848
	Pt	$\frac{17\ 03 \times 2}{195\ 23}$	17.45	1.2418
	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\frac{17\ 03 \times 2}{392\ 13}$	8.686	0.9388
	$\text{HCl}$	$\frac{18\ 04}{36\ 46}$	49.47	1.6944
	$\text{H}_2\text{SO}_4$	$\frac{18\ 04 \times 2}{98\ 08}$	36.79	1.5657
$\text{NH}_4$ . . .	$\text{NaOH}$	$\frac{18\ 04}{40\ 00}$	45.10	1.6542
	$\text{NH}_4\text{Cl}$	$\frac{18\ 04}{53\ 50}$	33.72	1.5279
	$(\text{NH}_4)_2\text{PtCl}_6$	$\frac{18\ 04 \times 2}{444\ 07}$	8.125	0.9099
	Pt	$\frac{18\ 04 \times 2}{195\ 23}$	18.48	1.2668
	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\frac{18\ 04 \times 2}{392\ 13}$	9.201	0.9638
$\text{NH}_4\text{Cl}$ . . .	$\text{HCl}$	$\frac{53\ 50}{36.46}$	146.7	2.1665
	$\text{H}_2\text{SO}_4$	$\frac{53\ 50 \times 2}{98\ 08}$	109.1	2.0378
	$\text{NaOH}$	$\frac{53\ 50}{40\ 00}$	133.8	2.1265
	$(\text{NH}_4)_2\text{PtCl}_6$	$\frac{53\ 50 \times 2}{444\ 07}$	24.10	1.3820

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B.	C. Weight of A represented by 100 grm. of B.	Log C.
$\text{NH}_4\text{Cl}$	Pt	$\frac{53.50 \times 2}{195.23}$	54.82	1.7389
$\text{NO}_2$	$\text{AgNO}_3$	$\frac{46.01}{169.89}$	24.69	1.3926
	$\text{KMnO}_4$	$\frac{46.01 \times 5}{158.03 \times 2}$	72.78	1.8620
	I	$\frac{46.01}{126.92}$	36.25	1.5593
	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{46.01}{158.1}$	29.10	1.4639
	$\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$	$\frac{46.01}{248.2}$	18.54	1.2680
$\text{NO}_3$	Fe	$\frac{62.01}{55.84 \times 3}$	37.02	1.5684
	HCl	$\frac{62.01}{36.46}$	170.0	2.2306
	$\text{H}_2\text{SO}_4$	$\frac{62.01 \times 2}{98.08}$	126.4	2.1019
	$\text{KNO}_3$	$\frac{62.01}{101.10}$	61.33	1.7877
	NaOH	$\frac{62.01}{40.00}$	155.0	2.1904
	$(\text{NH}_4)_2\text{PtCl}_6$	$\frac{62.01 \times 2}{444.07}$	27.93	1.4460
	Pt	$\frac{62.01 \times 2}{195.23}$	63.54	1.8030
	$\text{C}_{20}\text{H}_{15}\text{N}_4, \text{HNO}_3$	$\frac{62.01}{375.3}$	16.53	1.2183
Na	NaCl	$\frac{23.00}{58.45}$	39.34	1.5919
	$\text{Na}_2\text{SO}_4$	$\frac{23.00 \times 2}{142.05}$	32.38	1.5103
	$\text{Na}_2\text{Zn}_3\text{UO}_4, \text{—}$ $(\text{C}_2\text{H}_3\text{O}_2)_4, 6\text{H}_2\text{O}$	$\frac{23.00}{1538.1}$	1.495	0.1747
$\text{Na}_2\text{O}$	NaCl	$\frac{61.99}{58.45 \times 2}$	53.03	1.7245
	$\text{Na}_2\text{SO}_4$	$\frac{61.99}{142.05}$	43.64	1.6399
NaOH	Na	$\frac{40.00}{23.00}$	174.0	2.2404
	HCl	$\frac{40.00}{36.46}$	109.7	2.0402
	$\text{HNO}_3$	$\frac{40.00}{63.02}$	63.48	1.8027
	$\text{H}_2\text{SO}_4$	$\frac{40.00 \times 2}{98.08}$	81.58	1.9116
	$\text{KHSO}_4$	$\frac{40.00}{136.16}$	29.38	1.4681
$\text{Na}_2\text{CO}_3$	HCl	$\frac{106.00}{36.46 \times 2}$	145.3	2.1624

## Chemical Factors—continued

A Weight	B Weight as an Equivalent	Factor's Wt. of A to 1 Wt. of B	Factor's Wt. of A to 1 Wt. of B as a Percentage	Factor
$\text{Na}_2\text{CO}_3$	$\text{H}_2\text{SO}_4$	$\frac{106.00}{98.08}$	108.1	2.222
	$\text{KH}_2\text{SO}_4$	$\frac{106.00}{191.16 \div 2}$	28.92	1.582
$\text{NaCl}$	$\text{Ag}$	$\frac{58.45}{107.88}$	54.18	1.723
	$\text{AgCl}$	$\frac{58.45}{143.34}$	40.78	1.610
	$\text{AgNO}_3$	$\frac{58.45}{169.87}$	34.41	1.555
$\text{NaNO}_3$	$\text{KMnO}_4$	$\frac{69.00 \div 5}{158.04 \div 2}$	109.1	2.078
	$\text{I}$	$\frac{69.00}{126.92}$	54.36	1.753
	$\text{Na}_2\text{S}_2\text{O}_7$	$\frac{69.00}{158.1}$	43.64	1.629
	$\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$	$\frac{69.00}{248.2}$	27.80	1.440
$\text{Na}_2\text{S}_2\text{O}_8$	$\text{I}$	$\frac{158.1}{126.92}$	124.6	2.651
	$\text{K}_2\text{Cr}_2\text{O}_7$	$\frac{158.1 \div 6}{294.21}$	30.24	2.585
	$\text{KIO}_4$	$\frac{158.1 \div 6}{214.02}$	40.3	2.607
	$\text{KMnO}_4$	$\frac{158.1 \div 5}{158.04}$	100.0	2.002
	$\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$	$\frac{158.1}{248.2}$	63.71	1.562
$\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{S}_2\text{O}_7$	$\frac{248.2}{158.1}$	157.0	2.178
$\text{Na}$	$\text{NaO}$	$\frac{23.00}{29.00}$	79.3	1.257
	$\text{Na}_2\text{C}_2\text{H}_3\text{N}_2\text{O}_4$	$\frac{23.00}{52.04}$	44.22	1.777
	$\text{Na}_2\text{C}_2\text{H}_3\text{O}_4\text{NO}_2$	$\frac{23.00}{56.04}$	41.22	1.708
	$\text{NaSO}_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\frac{23.00}{148.0}$	15.54	1.152
	$\text{Ag}$	$\frac{23.00}{107.88 \div 2}$	43.5	1.431
	$\text{AgNO}_3$	$\frac{23.00}{169.87 \div 2}$	27.7	1.253
	$\text{KCN}$	$\frac{23.00}{117.04}$	20.0	1.220
$\text{F}$	$\text{KH}_2\text{PO}_4$	$\frac{19.00}{136.0}$	13.9	1.277



## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A. Formula Wt. of B.	C. Weight of A represented by 100 grm of B.	Log C.
P	$Mg_3P_2O_7$	$\frac{30.98 \times 2}{222.60}$	27.87	1.4451
	$(NH_4)_3PO_4 \cdot 12MoO_3$	$\frac{30.98}{1877.06}$	1.652	0.2181
	$P_2O_5 \cdot 24MoO_3$	$\frac{30.98 \times 2}{3597.96}$	1.724	0.2367
	$PbMoO_4$	$\frac{30.98}{367.2 \times 12}$	0.7040	1.8476
	NaOH	$\frac{30.98}{40.00 \times 23}$	3.372	0.5279
	$KH_2PO_4$	$\frac{141.96}{136.09 \times 2}$	52.17	1.7174
	$Mg_3P_2O_7$	$\frac{141.96}{222.60}$	63.79	1.8047
	$(NH_4)_3PO_4 \cdot 12MoO_3$	$\frac{141.96}{1877.1 \times 2}$	3.783	0.5778
	$P_2O_5 \cdot 24MoO_3$	$\frac{141.96}{3597.9}$	3.948	0.5963
	$PbMoO_4$	$\frac{141.96}{367.2 \times 24}$	1.612	0.2073
PO <sub>4</sub>	NaOH	$\frac{141.96}{40.00 \times 46}$	7.720	0.8876
	$KH_2PO_4$	$\frac{94.98}{136.09}$	69.80	1.8439
	$Mg_3P_2O_7$	$\frac{94.98 \times 2}{222.60}$	85.34	1.9312
	$(NH_4)_3PO_4 \cdot 12MoO_3$	$\frac{94.98}{1877.06}$	5.062	0.7044
	$P_2O_5 \cdot 24MoO_3$	$\frac{94.98 \times 2}{3598}$	5.282	0.7228
	$PbMoO_4$	$\frac{94.98}{367.2 \times 12}$	2.156	0.3337
	NaOH	$\frac{94.98}{40.00 \times 23}$	10.33	1.0140
	$K_2Cr_2O_7$	$\frac{207.2 \times 2}{294.2}$	140.9	2.1488
	$KMnO_4$	$\frac{207.2 \times 5}{158.0 \times 2}$	327.8	2.5156
	$PbO_2$	$\frac{207.2}{239.2}$	86.62	1.9376
Pb	$PbO_2 \cdot H_2O$	$\frac{207.2}{257.2}$	80.55	1.9061
	$PbCrO_4$	$\frac{207.2}{323.2}$	64.11	1.8060
	$PbMoO_4$	$\frac{207.2}{367.2}$	56.43	1.7515

## Chemical Factors—continued

A Sought	B Weighed as, or Equivalent to	Formula Wt. of A Formula Wt. of B	Weight of A represented by 100 gram of B	Log V
Pb	$\text{Pb}(\text{NO}_3)_2$	$\frac{207.21}{331.23}$	62.55	1.7962
		$\frac{207.2}{303.27}$	68.31	1.8345
PbO	$\text{K}_2\text{Cr}_2\text{O}_7$	$\frac{223.2 \times 2}{204.2}$	151.7	2.1811
		$\frac{223.2 \times 5}{158.0 \times 2}$	353.1	2.5470
	$\text{PbO}_2$	$\frac{223.2}{230.2}$	93.31	1.9699
		$\frac{223.2}{257.2}$	86.77	1.9384
	$\text{PbO}_2, \text{H}_2\text{O}$	$\frac{223.2}{323.2}$	69.06	1.8392
		$\frac{223.2}{307.2}$	66.78	1.7838
	$\text{PbSO}_4$	$\frac{223.2}{303.27}$	73.60	1.8660
		$\frac{685.6}{120.9 \times 2}$	270.1	2.4315
	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{685.6}{158.1 \times 2}$	216.8	2.3361
		$\frac{685.6}{218.2 \times 2}$	158.1	2.1993
PbO <sub>2</sub>	I	$\frac{239.2}{126.9 \times 2}$	94.23	1.9742
		$\frac{239.2}{158.1 \times 2}$	76.61	1.8788
	$\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$	$\frac{239.2}{218.2 \times 2}$	48.19	1.6820
		$\frac{32.06}{213.42}$	13.73	1.1377
S	$\text{H}_2\text{SO}_4$	$\frac{32.06}{98.08}$	32.69	1.5141
		$\frac{64.06}{213.42}$	27.41	1.4385
SO <sub>2</sub>	$\text{BaSO}_4$	$\frac{64.06}{126.9 \times 2}$	25.24	1.4020
		$\frac{64.06 \times 2}{214.62}$	69.86	1.7772
	I	$\frac{64.06}{158.1 \times 2}$	20.26	1.3066
		$\frac{64.06}{218.2 \times 2}$	12.00	1.1468
	$\text{BaSO}_4$	$\frac{80.06}{233.42}$	34.30	1.5354

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A. Formula Wt. of B.	C. Weight of A represented by 100 grm. of B.	Log C.
SO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	80.06	81.63	1.9118
		98.08		
		80.06		
SO <sub>2</sub>	NaOH	40.00 × 2	100.1	2.0003
		98.06		
		233.42		
SO <sub>2</sub>	BaSO <sub>4</sub>	98.06	41.15	1.6144
		233.42		
		98.06		
SO <sub>2</sub>	CuSO <sub>4</sub> , 5H <sub>2</sub> O	249.7	38.47	1.5851
		98.06		
		98.08		
SO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	98.06	97.94	1.9910
		98.08		
		98.06		
SO <sub>2</sub>	NaOH	40.00 × 2	120.1	2.0794
		112.12		
		233.42 × 2		
S <sub>2</sub> O <sub>2</sub>	BaSO <sub>4</sub>	112.12	24.02	1.3805
		233.42 × 2		
		112.12		
Sb	I	126.92	88.34	1.9462
		121.76		
		126.92 × 2		
Sb	KBrO <sub>3</sub>	121.76 × 3	218.8	2.3400
		167.01		
		121.76 × 5		
Sb	KMnO <sub>4</sub>	158.03 × 2	102.6	2.2847
		121.76		
		158.1 × 2		
Sb	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	121.76	38.51	1.5855
		158.1 × 2		
		121.76		
Sb	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O	248.2 × 2	24.53	1.3897
		121.76 × 2		
		307.52		
Sb	Sb <sub>2</sub> O <sub>3</sub>	121.76 × 2	78.98	1.8975
		339.70		
		121.76		
Sb	K(SbO)C <sub>6</sub> H <sub>4</sub> O <sub>4</sub>	324.93	37.47	1.5737
		28.06		
		60.06		
Si	SiO <sub>2</sub>	76.06	46.93	1.6715
		60.06		
		76.06		
SiO <sub>2</sub>	SiO <sub>2</sub>	60.06	126.5	2.1022
		118.70		
		150.70		
Sn	SnO <sub>2</sub>	118.7	78.81	1.8966
		150.70		
		118.7		
Sn	I	126.92 × 2	40.76	1.6600
		118.7 × 3		
		167.01		
Sn	KBrO <sub>3</sub>	118.7 × 3	213.2	2.3288
		118.7		
		214.02		
Sn	KIO <sub>3</sub>	118.7	166.4	2.2212
		214.02		
		118.7		
Sn	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	118.7	37.54	1.5754
		150.70		
		118.7 × 2		

## Chemical Factors—continued

A. Sought.	B. Weighed as, or Equivalent to.	Formula Wt. of A Formula Wt. of B	C. Weight of A represented by 100 grm of B.	Log C.
Sn . .	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$\frac{118.7}{248.2 \times 2}$	23.91	1.3786
Sr . .	$\text{SrSO}_4$	$\frac{87.63}{183.69}$	47.71	1.6786
SrO . .	$\text{SrSO}_4$	$\frac{103.63}{183.69}$	56.42	1.7514
Ti . .	$\text{TiO}_2$	$\frac{47.90}{79.90}$	60.05	1.7785
	Fe	$\frac{47.90}{55.84}$	85.78	1.9334
	$\text{K}_2\text{Cr}_2\text{O}_7$	$\frac{47.90 \times 6}{294.21}$	97.69	1.9898
W . .	$\text{WO}_3$	$\frac{183.92}{231.92}$	79.32	1.8993
Zn . .	$\text{ZnO}$	$\frac{65.38}{81.38}$	80.34	1.9049
	$\text{ZnHg}(\text{CNS})_4$	$\frac{65.38}{498.37}$	13.12	1.1180

# GENERAL INDEX

The most important

Analysis

is,

And

tubes

Alumimetry, 118-138

Adams' method for determining milk fat, 378

Adsorption indicators, 101

Air, determination of carbon dioxide in, 484

determination of oxygen in, 471

specific gravity and other data, 516

Air-bath, 36, 443

Air-drying, 256, 317, 327

Air-oven, 28

Albuminoid ammonia, in water, 353, 372

Alcohol, in beer and wine,

Alk

Alk... in limestone and silicates, determination of, 271, 277

in soap, 420

separation from other metals, 79, 80, 271, 278

Alkalimetry, 118-138

Alumina, crucibles, 48

Aluminium, analysis of alloys, and results, 295, 491

commercial, analysis of, 295

determination of, as oxide (g), 64

as phosphate (g), 65

by hydroxyquinoline (g), 65

by hydroxyquinoline (v), 171

colorimetrically, 241

in presence of iron, 270

in steel, 312

in water, 242

iron in, electrometrically, 216

nephelometrically, 250

separation, general, 270, 294, 295, 300

from iron, 65, 270, 300

from titanium, 294

other examples, 316

Aluminon, 241

Alundum, crucible, 44

Amalgam, zinc, preparation of, 148

Ambler's apparatus for gas analysis, 482

direct gravimetric determination

of, 82

volumetric determination of,

183

determination of, as

chloroplatinate (g), 82

as platinum (g), 84

by absorption, 480

results, 350, 372

separation from metals by

distillation, 82

specific gravity table, 506

Ammonium aurine tricarboxylate, 241

molybdate, preparation of

reagent, 79

salts, determination of, by

nitrometer, 480

sublimation, 107

analytical reagents, 517

Angström unit, 514

Anti-logarithm tables, 554

Antimony, determination of, as

sulphide and oxide (g), 93, 96

by iodine (v), 168

by potassium bromate (v), 182

by potassium iodate (v), 181

by potassium

permanganate (v), 283, 290

colorimetrically, 244

in white metals, 290

precipitation of, in hydrogen

sulphide group, 283

pentasulphide, conversion to

trisulphide, 95

Aperiodic balance, 3

[illegible]

- Crum's method for determining nitrate and nitrite**, 358
- Cupferron**, use of, 303, 317
- Cupro-nickel alloys**, analysis of, and results, 289, 491
- Cupron reagent for molybdenum (g)**, 315
- Cuprous chloride solution**, for gas analysis, 469
- Cyanide**, determination of, as silver cyanide or as silver (g), 73  
by silver nitrate (v), 195
- Cyanogen**, determination of, as silver cyanide (g), 73
- Density bottle**, 14, 17
- Density, relative**. See **Specific gravity**.
- Desiccants**, 30
- Desiccation**, 25-31
- Desiccator, vacuum**, 31
- Devarda's alloy**, 84, 133
- Dichromate**, determination of, by iodine (v), 165  
preparation of standard solution of, 140
- Diethylthiocarbamate reagent for copper**, 239
- Di-iodo-eosin**, as adsorption indicator, 192
- Di-iodofluorescein**, as adsorption indicator, 192
- Dimethylglyoxime reagent**,  
determination of  
nickel  
colorimetrically, 241  
gravimetrically, 62
- Diphenylamine**, as oxidation-reduction indicator, 145
- Diphenylbenzidine**, as an indicator, 200
- Dissolved gases in water**, determination of, 369, 480
- Dolomite**, analysis of, and results, 268, 491
- Double salts**, preparation of, 53, 55
- Drop-ratio method for  $P_n$**   
determinations, 208
- Dry assay**, 340-347
- Drying**, 25-31  
agents, 30
- Vapour density process**, 457
- Eggertz's method for determination of carbon in steel**, 247, 257
- Electrical units**, 516
- Electrode**, calomel, 211  
hydrogen, 209  
potentials of metals, 225  
Sand's rotating, 227  
stationary, 226
- Electrodeposition analysis**, 225-233  
micro-methods, 230
- Electrolytic determinations**, 205-233, 252
- Electrometric titrations**, 205-220
- Entry**, example of, in note-book, 62, 128
- Enzymes**, determination of  
nephelometrically, 251
- Eosin**, as adsorption indicator, 192
- Equivalent weight of organic acid**,  
determination of, 446  
of organic base, determination of, 447
- Equivalents**, 115
- Errors in gravimetric analysis**, 59  
in volumetric analysis, 125  
of meniscus, 464  
statistical evaluation of, 487
- Eschka mixture**, 319
- Precautions during**, 35
- Expansion of water**, table, 496
- Factor quantity**, 303
- Factors for gravimetric and volumetric analysis**, table of, 521
- Fahrenheit scale**, conversion of, 514
- Fat in butter**, determination of, 383  
in milk, calculation of, 379  
determination of, and results, 375-379
- Fats, oils and waxes**, examination of, 401-426  
table of characteristics, 508-513
- Fatty acids**, determination of, 384, 413, 419, 422
- Fehling's solution**, preparation of, 394
- Felspar**, analysis of, and results, 276, 491, 494
- Ferric salts**, determination of,
- Ferrous ammonium sulphate**,  
preparation of, 56  
oxalate, determination of, 158  
phenanthroline, 144, 145
- Ferro-vanadium**, analysis of, by  
electrometric method, 218
- Fertilisers**, evaluation of, and results, 326-332, 493, 494
- Filter for carbon in steel**, 306
- Filter-crucibles**, 42-45





- Hydrogen peroxide, determination of,  
by ceric sulphate, 162  
by iodine, 179  
by nitrometer, 482  
by potassium permanganate, 159
- Hydrogen sulphide, determination of,  
by iodine, 168  
oxidation of, by hydrogen peroxide, 70
- Hydrometer, 18  
scales, 513
- Hydroxyquinoline, bromination of, 171
- Hypochlorites, determination of, by  
arsenious oxide method, 181  
by ferrous salt method, 152, 154
- Iceland spar, use of, in standardising  
hydrochloric acid, 127
- Ignition of precipitates, 46-53
- Indicators, acid-alkali, 118, 206, 237  
adsorption, 191  
for  $P_n$ , list of, 493  
oxidation-reduction, 143-145  
universal, 495
- Inversion of cane sugar, 394, 396, 399
- Iodate, determination of,  
iodometrically, 176  
in presence of periodates, 177  
preparation and use of standard  
solution, 180
- Iodides, determination of, as silver  
iodide (g), 72  
by electrometric method, 220  
by potassium iodate (v), 180  
by silver nitrate (v), 194  
by thiocyanate (v), 198  
in presence of bromides and  
chlorides, 193, 220  
of chlorides, 72  
of iodine, 180
- Iodide-iodate, standard solution of, 180  
use of for standardisation, 129,  
140, 180
- Iodide-starch solution, preparation of,  
215
- Iodine, determination of, as silver  
iodide (g), 74  
by potassium iodate (v), 180  
by sodium arsenite (v), 166,  
184  
by thiosulphate (v), 163  
in organic compounds,  
441-445  
in presence of iodides, 181  
purification of, by sublimation, 57  
standard solution, preparation and  
use of, 162  
value of fats and oils, 412,  
508-513
- Iron, determination of, as ferric  
oxide (g), 64  
by ceric sulphate 162
- Iron, determination by permanganate  
(v), 155, 157  
in presence of  
hydrochloric acid (v),  
157  
by potassium dichromate (v),  
145, 149  
by titanous chloride (v), 187  
colorimetrically by ferro-  
cyanide, 237  
by thiocyanate, 238  
electrometrically, 214, 216  
iodometrically (v), 179  
in aluminium, determination of,  
electrometrically, 216  
in glass, determination of,  
colorimetrically, 237  
in ores. See Iron ores.  
in presence of aluminium, 270  
in water, determination of, 368,  
374  
colorimetrically, 237  
in zinc, determination of,  
colorimetrically, 237  
oxidation of, to ferric state, 187,  
270  
precipitation of, by cupferron, 294,  
316  
preparation of ferrous solution,  
140  
reduction by stannous chloride,  
116  
by sulphurous acid, 140  
by zinc, 147  
by zinc amalgam, 148  
separation from all metals except  
molybdenum, 312  
from aluminium, 294  
from calcium and  
magnesium, 270  
from manganese, nickel,  
cobalt and zinc, 300  
from titanium, 293  
separations, other examples, 316
- Iron ores, analysis of, and results, 149,  
157, 187, 299, 491, 492  
titaniferous, analysis of, 187,  
302  
evaluation of chromic ore, 258
- Iron and steel, analysis of, and results,  
303-317, 400
- Jacket, hot water, 54
- Jena, crucible, 44
- Jones reductor, 147, 148, 189
- Kirschner value of a fat, 387
- Kjeldahl's determination of nitrogen,  
435  
micro-method, 436
- Koettstorfer value for fats and oils, 409,  
508-513
- Lane and Eynon's method for  
determination of sugars, 395

- Lawrence Smith's method for determination of alkalis, 271  
 Lead, action of, on water, 243, 367  
   assay of silver in, 312  
   determination of, as chromate (g), 73  
     as chromate (v), 154, 172  
     as sulphate (g), 74  
   by ammonium molybdate (v), 201  
   by dry assay, 341  
   by electrolysis, as peroxide, 233  
   by potassium permanganate (v), 150  
     colorimetrically, 242  
   in brass, determination of, 286  
   in galena, determination of, and results, 282  
     by dry assay, 341  
   in glass, determination of, 278  
   in lead carbonate, determination of, by dry assay, 342  
   in ore, determination of, by ammonium molybdate, 201  
   in oxides, determination of, by dry assay, 312  
   in water, determination and effect on, 243, 367, 374  
   in white metals, determination of, and results, 291, 491  
   separation, general, 280  
     from antimony and tin, 291  
     from copper, 292  
     from silica, 280  
     from sulphur, 284  
     dithizone method, 243  
 Lead dioxide, evaluation of by permanganate (v), 159  
   iodometrically (v), 176  
 Leeds' method of soap analysis, 422  
 Lias-lime, analysis of, and results, 274, 494  
 Liebermann-Storch reaction, 418  
 Lime, analysis of, and results, 268, 274, 332, 494  
   determination of free lime, 273  
 Limestone, analysis of, and results, 268, 274, 332, 491  
 Liquid, determination of boiling-point of, 20-22  
   density of, 15-18  
   of  
     tannin, 337  
 Lunge nitrometer, description and use of, 477  
   calibration of, 465  
 Magnesia mixture, preparation of, 78  
 Magnesian limestone, analysis of and results, 268, 491  
 Magnesium, determination of, as phosphate or pyro-  
   precipitation of, as magnesium ammonium phosphate, 76  
   separation from alkaline earths, 78  
     from calcium, 78, 271  
     from iron and aluminium, 270  
     from nickel, zinc, etc., 278  
 Magnesium phosphate, determination of, by uranyl nitrate (v), 203  
   potassium sulphate, preparation of, 56  
 Manganese, determination of, as phosphate and pyrophosphate (g), 75  
   by bismuthate process (v), 267  
   colorimetrically, 240  
   in iron and steel, and results, 311, 490  
     colorimetrically, 240  
   in steel, by electrometric method, 217  
   in limestone, 270  
   in ores, 267  
   ores, evaluation of, 266  
   precipitation of, as manganese ammonium phosphate, 75  
   separation from aluminium, iron and titanium, 300  
     from calcium and magnesium, 270  
     from zinc, 281, 284  
   in iron and steel analysis, 311  
   sulphate, use of with permanganate, 157  
 Manganese dioxide, determination of, iodometrically (v), 174  
   by ferrous salt method (v), 267  
   by oxalic acid (v), (g), 267, 482  
 Manganese spar, analysis of, 269  
 Mansfield's method for determination of copper, 197, 262  
 Manures, evaluation of, and results, 326-332, 493, 494  
 Margarine, 388  
 Maumené reaction in fats and oils, 405, 508-513  
 McNichol's method for determination of resin in soap, 421  
 Mean molecular weight of fats and oils, 414  
 Memoranda, useful, 516

- Meniscus**, error of, 111, 464  
**Mercurous nitrate** separation, 317  
**Mercury**, determination of, as metal, 98, 260  
     as chloride (g), 100  
     as sulphide (g), 100  
     by distillation (g), 98, 250  
     by thiocyanate (v), 199  
     reduction to mercurous state, 100  
     weight of 1 c.c. of, 516  
**Mercury ore**, evaluation of, 259  
**Metals** in water, detection and determination of, 366  
**Methane**, determination of, 474  
**Methyl orange**, 119, 172  
     necessity for reference standard, when using, 124  
**Methyl red**, 120, 125  
**Metric units**, and conversion to, 514  
**Meyer's method** for determination of vapour density, 454  
**Micro-chemical methods**, 250  
     balance, 4  
     burette, 114  
     combustion of organic substances, 435  
     electrodeposition, 230  
     filtration, 45  
     gas-analysis, 482  
     Kjeldahl nitrogen determination, 436  
     pipette, 111  
**Milk**, analysis of, 375-382  
     water in, 379, 380  
**Millilitre**, definition, 106  
**Mineral constituents** in water, determination of, 368  
     oils in fats and oils, determination of, 411  
     oils and waxes, analysis of, and results, 421-425, 510  
     phosphates, analysis of, and results, 327, 493, 494  
**Mobility of ions**, table of, 221  
**Mohr units of volume**, 514  
**Moisture** in gas, correction for, 461, 499  
**Molecular solution**, definition of, 116  
**Molecular weights**, determination of, by boiling-point method, 451  
     by Dumas' method, 457  
     by freezing-point method, 448  
     by Rast's method, 450  
     by Victor Meyer's method, 454  
     of organic acids and bases, determination of, 446, 447  
**Molybdate**, ammonium, preparation of solution of, 79  
     method for determination of phosphates (g), 78, (v) 136  
**Molybdenum**, determination of, in steel, 314  
     cupron method (g), 315  
**Molybdenum**, separation of, from iron and manganese, 314  
     from other metals, 317  
**Mortar**, analysis of, and results, 274, 494  
**Mortar**, steel percussion, 23  
**National Physical Laboratory**  
     standards for volumetric glassware, 498  
**Nephelometric analysis**, 249-251  
**Nessler tubes**, 235, 350  
**Nessler's reagent**, preparation of, 246, 351  
**Neutralisation of solutions**, 118, 194  
     value of fats and oils, 414, 508  
**Nickel**, determination of, by dimethyl glyoxime (g), 62, 241  
     by electrolysis, 231  
     by potassium cyanide (v), 196  
     by salicylaldehyde (g), 289  
     colorimetrically, by dimethylglyoxime, 241  
     in German silver, determination of, 289  
     in iron and steel, determination of, 312  
     separation from aluminium and iron, 62  
     from aluminium, iron and titanium, 300  
     from copper, cobalt manganese and zinc, 62  
     from other metals, 312  
     from other metals, as dimethylglyoxime compound, 62  
     from zinc, 284  
     in iron and steel analysis, 310  
     vessels, use of, 48  
**Nitrate**, determination of, as ammonium chloroplatinate (g), 84  
     as nitron nitrate, 85  
     by nitron (g), 85  
     by potassium dichromate (v), 151  
     by reduction to ammonia (v), 133  
     by titanous chloride (v), 188  
     colorimetrically, 245, 360  
     in water, determination of, and results, 358, 360, 373  
     as ammonia by zinc-copper couple, 359  
     by gasometric method, 358, 479  
     colorimetrically, by diphenylamine sulphonic acid, 245  
     by phenolsulphonic acid, 360  
**Nitric acid**, reduction of, by Devarda's alloy, 84  
     specific gravity table, 505

- Nitric oxide, determination of, 478  
 Nitrites, determination of, by  
     chloramine-T (v), 184  
     by ferrous salt method (v),  
         152  
     by potassium permanganate  
         (v), 160  
     colorimetrically, 245, 357  
     in water, determination of, and  
         results, 357-360, 373  
 Nitrogen gas, determination of, 471,  
     474  
     in an organic compound,  
         determination of, 330, 435-  
         441  
     in manures, determination of,  
         and results, 330, 494  
     in water as nitrate and  
         nitrite, determination of,  
         357, 360  
     oxides in nitrous vitriol,  
         determination of, 478  
     weight of 1 ml., 516  
 Nitrogenous manures, evaluation of,  
     330  
 Nitrometer, description and use of, 358,  
     477  
 Nitron reagent for nitrates, 85  
 Nitrous oxide, determination of, 472  
 Nitrous vitriol, examination of, 478  
 Normal solutions, 115, 121-127  
     volume of gases, calculation of,  
         461  
 Note-book, examples of entries in, 60,  
     62, 128  
  
 Oils, fats and waxes, table of  
     characteristics, 389, 508-513  
     colour tests for, 417  
     examination of, 401-418, 421-426  
 Olefines, determination of, 471  
 Orange III, 119  
 Organic analysis, 427-445  
     combustion for carbon and  
         hydrogen, 427-435  
     for halogens, 441  
     for nitrogen, 435  
 Organic compounds, determination of  
     halogens in, by  
         Carus' method, 442  
     by Stepanov's method,  
         444  
     nitrogen in, by Kjeldahl's  
         method, 435  
     sulphur and phosphorus in,  
         445  
 Organic matter in water, determination  
     of, and results, 350, 372  
 Original gravity of beer, determination  
     of, 391  
 Orthoclase, analysis of, and results,  
     275, 494  
 Orthophthalate, potassium hydrogen,  
     for standardisation of alkalis,  
         127  
 Orthophthalate, preparation of, 207  
 Oven, air, 28  
     for maintaining constant  
         temperature, 29  
     steam, 26  
 Oxalic acid, use of, in standardisation  
     of alkalis, 127  
 Oxidation, prevention of, 48  
 Oxidation-reduction indicators, 143-  
     145, 200  
     reactions, 189-190  
         in iron and steel analysis, 316  
         theory of, 214-216  
 Oxine, use of in gravimetric analysis,  
     65, 77, 171  
 Oxygen, average percentage in air,  
     471  
     demand of water, determination  
         of, 371  
     process of determination of organic  
         matter in water, 354  
 Oxygen in water, determination of, by  
     manganese salt, 369  
     degree of saturation, 371  
  
 Palladinised asbestos, preparation of,  
     472  
 Palmitate method for the hardness of  
     water, 364  
 Parting gold and silver, 345  
 Penfield and Brush, determination of  
     water, 94  
 Perchlorates, determination of, as  
     silver chloride (g), 73  
     reduction to chloride, 73  
 Percussion mortar, 23  
 Periodates, determination of, 177  
 Permanent hardness of water,  
     determination of, 362, 365, 373  
 Permanganate, potassium,  
     preparation and use of  
         standard solution, 155  
     process for determination of  
         tannin, 337  
         of organic matter in  
             water, 350, 372  
 Permanganates, determination of, by  
     nitrometer, 482  
     volumetrically, 155, 156, 165,  
         482  
 Persulphates, determination of,  
     by oxalic acid (v), 160  
     by potassium permanganate  
         (v), 160  
     by titanous chloride (v), 188  
 Pettenkofer's determination of carbon  
     dioxide in air, 484  
 Pewter, analysis of, 290

- P<sub>H</sub>**, definition of, 118, 203, 205, 237  
 measurement of, by electrometric method, 208  
 by indicators, 118, 206  
 list of indicators, 495
- Phenanthroline**, ferrous, 144, 145
- Phenol**, determination of,  
 iodometrically, 171
- Phenolphthalein**, use of, 119
- Phenol red**, 237
- Phenolsulphonic acid**, use of, in determination of nitrates, 360
- Phenosafranine**, as adsorption indicator, 192
- Phosphates**, determination of, as ammonium phosphomolybdate (g), 78  
 as magnesium pyrophosphate (g), 77  
 as phosphomolybdic anhydride (g), 78  
 by uranyl salts (v), 202  
 by volumetric molybdate process (v), 186  
 colorimetric method, 246  
 nephelometric method, 250  
 mineral, analysis of, and results, 327, 493, 494
- Phosphatic manures**, analysis of, and results, 327, 493, 494
- Phosphor-bronze**, analysis of, and results, 287
- Phosphoric acid**, determination of, in mixture of acids (v), 137
- Phosphorus acid**, preparation of, 100
- Phosphorus**, determination of, as lead molybdate (g), 310  
 in bronze, 287  
 in coal, 320  
 in iron and steel, and results, 310, 490  
 in organic compounds, 445  
 separation from arsenic, 78  
 from certain elements, 317
- by
- Pipettes**, calibration and use of, 109  
 Hempel, 472  
 micro-, 111  
 times of outflow, 498
- Platinum crucible**, cleaning and conditions of use, 46  
 electrodes, preparation of, 209
- Poisonous metals in water**, detection and determination of, 360
- Polarimeter**, use of, in determination of sugars, 397
- Polarograph**, 252
- Polenske values for butter fat**, 384, 386, 413, 508
- Policeman**, 39
- Porcelain crucible**, conditions of use, 48
- Porous plate**, use of, in drying, 55
- Portland cement**, analysis of, and results, 274, 493
- Potash bulbs**, for organic combustion, 430  
 manures, evaluation of and results, 331, 494  
 soaps, analysis of, 421  
 specific gravity table, 507
- Potassium**, determination of, as platinum (g), 81  
 as platinichloride (g), 80  
 as potassium perchlorate (g), 82, 331  
 as sulphate (g), 82  
 indirectly in presence of sodium 272  
 in glass, 278  
 in limestone and silicates, determination of, and results, 271, 491, 494  
 in manures, 331  
 separation from other metals, 80, 81, 82, 278  
 from sodium, 80, 272
- Potassium Salts**  
 Alum, preparation of, 55  
 Antimonyl tartrate, preparation of, 57  
 Bicarbonate, use of, for standardisation of acids, 125  
 Bisulphate, use of, for standardisation of alkalis, 127  
 Bromate, preparation and use of standard solution, 182  
 Chromate, as an indicator, 193  
 Cyanide, preparation and use of standard solution, 196  
 Dichromate, preparation and use of standard solution, 139-143  
 Ferricyanide, use of, as external indicator, 139  
 Ferrocyanide, preparation and use of standard solution, 200  
 solution, standardisation of, electrometrically, 219  
 Hydrogen orthophthalate, preparation of, 207  
 use of, for standardisation of alkalis, 127  
 Hydrogen tartrate, for standardisation of alkalis, 127  
 Hydroxide solution, for gas analysis, 469  
 specific gravity table, 507
- Iodate**, preparation and use of standard solution, 180  
 use of, in neutralising a solution, 129, 132
- Iodide**, use of, in volumetric analysis, 169-179
- Magnesium sulphate**, preparation of, 55
- Oxalate**, identification of (v), 137
- Permanganate solution**, preparation and use of, 155

*Potassium Salts*

- Permanganate solution, standardisation by ferrous salt, 155
  - by oxalic acid, 156
- Persulphate, evaluation of (*v*), 138
- Tetroxalate, use of, for standardisation of alkalis, 127
- Thiocyanate, preparation and standardisation of solution, 108
- Potentiometric titrations, 205-220
- Powdering, process of, 23
- Precipitates, drying of, 46
  - filtration of, 37-45
  - ignition of, 46-53
  - washing of, 37
- Preparation of pure compounds, 53-57
- Preservatives in butter, 383
  - in milk, 381
- Pressure on gas, correction for, 461
- Prismatic-reflecting balance, 4
- Procter extractor, 331
- Proof spirit, percentage of, from specific gravity tables, 500, 501
- Proteins, nephelometric analysis of, 251
- Pure compounds, preparation of, 53-57
- Pyknometer, 17
- Pyridine thiocyanate method for the
  - 174, 266, 493

- Quartering, process of, 251
- Quartz, dry assay of gold, 341
- Quick-lime, analysis of, and results, 268, 491

- Raoult's method for determination of molecular weights, 448
- Rast's method for determination of molecular weights, 450
- Reagents, analytical,
  - for gas analysis, 469
  - list of bench, 517
- Réaumur scale, conversion to Centigrade scale, 513
- Red lead, evaluation of, by dry assay, 340

- R
- R
- Reference books, list of, 518
  - tables for general analysis, 490-513, 521
- Refractive Index of oils, 406
- Reichert-Meißel value for fats, 384, 413, 508-513
- Reichert-Polenske method for volatile fatty acids, 384, 385, 413
- Relative Density. *See* Specific Gravity.

- Resin acids in soap, determination of, 421

- Rider, use of, 6
- Rose Bengal, as adsorption indicator, 192
- Röse-Gottlieb method for fat in milk, 376
- Rosenhain calorimeter, 321
- Rose's crucible, 48
- Rules for working, 57

- Saccharimeter, 398
- Safranine. *See* Phenosafranine.
- Salt, determination of, in beer, 393
  - in butter, 382
- Salts, preparation of pure, 53-57
- Samples analysed, 489
  - collection of, for gas analysis, 470
  - for water analysis, 348
- Sampling metals and alloys for analysis, 256
  - ores, etc., for analysis, 23, 254
  - water for analysis, 348
- Sand-bath, 35
- Saponification value of fats and oils, 400, 508-513
- Scale's method for the determination of free lime, 273
- Schiff nitrometer, 439
- Schmidt method for fat in milk, 375
- Schrotter's apparatus for determination of carbon dioxide, 90
- Scorification, process of, 343
- Semi-normal solution, definition of, 115
- Separations of use in analysis of iron and steel, 316
- Sesamé oil, test for, 417
- Sieves, British Standard, 24
- Silica, determination of, in a soluble silicate (*g*), 100, 269
  - in an insoluble silicate (*g*), 274
  - soluble silica, 274, 368
  - removal of, by fuming with hydrofluoric acid, 101
  - separation from lead, 280
  - vessels, conditions of use, 48
- Silicates, analysis of, if soluble in acids, and results, 100, 274, 491
  - if insoluble in acids, and results, 275, 491
- Silicon, determination of, in aluminium alloys, 297
  - in iron and steel, and results, 309, 490
  - separation from certain elements, 317
- Silver, determination of, as silver chloride (*g*), 74
  - by dry assay, 344
  - by potassium thiocyanate (*v*), 197

Silver, determination of, by sodium chloride (v), 191, 193  
 and adsorption indicator (v), 191  
 conductivity method, 224  
 method of 590  
 60,  
 in galena, determination of, by dry assay, 341-344  
 in lead, determination of, by dry assay, 342  
 in plate, determination of, by dry assay, 342  
 residues, recovery of, 195  
 separation from copper, 257  
 vessels, 48  
 Soap, analysis of, 401, 418-421  
 Leeds scheme, 422  
 preparation of standard solution, 362  
 Soda, specific gravity table, 506  
 determination of 82  
 sulphate (g), 10  
 zinc uranyl acetate salt (g), 80  
 in glass, 278  
 in limestone and silicates, determination of, and results, 271, 491, 493  
 indirect determination of, in  
 125  
 Sodium Salts  
 Acetate, conductometric determination of, 224  
 Arsenite, preparation of standard solution, 167  
 Bicarbonate, determination of, in presence of sodium carbonate, 130  
 transformation to carbonate, 122  
 Carbonate, determination of, in presence of sodium bicarbonate, 130, 265  
 hydroxide, 129, 265  
 of water in, 137, 269  
 from sodium bicarbonate, 122  
 preparation of normal solution, 122  
 Chloride, preparation of pure, 50  
 standard solution, 191

in presence of sodium carbonate, 129  
 conductometric method, 223  
 potentiometric method, 212  
 preparation of normal solution, 126  
 of solution free from carbon dioxide, 126  
 specific gravity table, 506  
 Nitrate, determination of, by nitrometer, 358, 479  
 Sesquicarbonate, determination of, 130  
 Thiosulphate, preparation of standard solution, 162  
 Solder, analysis of, 290  
 Solids, determination of melting-point of, 18-20  
 in water, 349, 350  
 not fat, in milk, 379  
 powdering of, 23  
 solution of, 31  
 specific gravity, determination of, 12-14  
 Solubility, determination of, 32  
 Solution of solids, process of, 32  
 Solutions, standard, 106, 115, 121, 129  
 molecular, 116  
 normal, 115, 122-129  
 storage of, 116, 125, 186  
 nd  
 Baumé degrees, 513  
 definition of, 12  
 of air, 316  
 of fats, oils and waxes, 508-513  
 of heavy solids, determination of, 12  
 of hydrogen, 516  
 of light solids, determination of, 13  
 of liquids, determination of, 15-18  
 of milk, 375  
 of powders, determination of, 14  
 of solids soluble in water, determination of, 14  
 tables, 500-507  
 analysis 231  
 392  
 390  
 by,  
 31, 31, 40  
 Sprengel tube, 17  
 modified form, 18  
 Standard acidic substances, 120  
 basic substances, 125

- Standard solutions, 106, 115, 121, 129  
correlation of volumetric, 128  
storage and preservation of, 116, 164, 186
- Stannous chloride, use of, as a reducing agent, 146
- Starch solution, preparation of, 164
- Starch-iodide solution, preparation of, 245
- Statistical evaluation of errors, 485
- Steam-oven, simple, 25
- Steam-ovens and water-still combined, 27
- Steel, analysis of, and results, 247, 303-317, 490  
percussion mortar, 23
- Stepanov's method for determination of halogens in organic compounds, 444
- Still for distilling water, 27  
for determination of alcohol in beer, 391
- Storage of standard solutions, 116, 135, 164, 186
- Strontium, determination of, as sulphate (g), 67
- Sublimation, purification by, 57
- Substitution, weighing by, 9
- Sugar, analysis and determination of, 393-400
- Sulphates, determination of, as barium sulphate (g), 65; (v), 174, 224  
sulphate (g), 70  
by potassium iodate (v), 182  
iodometrically (v), 169
- Sulphur, determination of, as barium sulphate (g), 68; (v), 174, 224  
volumetrically, 307  
in blende, determination of, and results, 68, 282, 492  
in coal, determination of, 319  
in iron and steel, determination of, and results, 307, 490  
in oil, determination of, 425  
in organic compounds, determination of, 445  
in sulphides, determination of, 68-70  
in zinc-blende, determination of, and results, 68, 282, 492  
conversion of, to ferrous sulphide, 69  
oxidation of, by bromine, 68  
by hydrogen peroxide, 69  
by nitric acid, 69  
by potassium nitrate, 68
- Sulphur dioxide, determination of, iodometrically (v), 169  
use of, as a reducing agent, 146
- Sulphuretted hydrogen, determination of, iodometrically (v), 168, 307  
oxidation of, by hydrogen peroxide, 69
- Sulphuric acid, preparation of normal solution, 123  
specific gravity table, 502, 503
- Sulphurous acid, determination of, iodometrically (v), 169
- Superphosphate of lime, analysis of, and results, 327, 493, 494
- Supports for filter, 42
- Suspended matter in water, determination and examination of, 340
- Swings, weighing by, 7, 9
- Syphon aspirator, 86
- Tables, for reference, 518
- Tabular form, use of in calculations, 128
- Tannin, determination of, 332, 336  
in tea, determination of, 400  
use of, as indicator, 202
- Tanning materials, extraction and evaluation of, 332-340
- Tartar emetic, purification of, 57  
determination of, 168
- Tartrazine as adsorption indicator, 192
- Tea, partial paralysis of, 399
- Teclu burner, 50
- Temperature of gas, correction for, 461
- Temporary hardness of water, determination of, 364, 365
- Tension of aqueous vapour, table of, 499
- Tetrahydroxy quinone as indicator, 174
- Tetrathionates, determination of, by potassium iodate (v), 182
- Theme in tea, determination of, 400
- Thermometer, correction of reading, 20
- Thermometric scales, conversion of, 513
- Thiocyanates, determination of, by potassium iodate (v), 182  
preparation and use of standard solution, 197
- Thiosulphates, determination of, as barium sulphate (g), 70  
by potassium iodate (v), 182  
preparation and use of standard solution, 162-171
- Thomas' phosphate, analysis of, and results, 327, 493, 494
- Thompson's calorimeter, description of, 321
- Times of outflow for burettes and pipettes, 498
- Tin, determination of, as dioxide (g), 97  
by chloramine-T (v), 184  
by electrolysis, 233  
by potassium bromate (v), 182



- Tin**, determination of, by titanous chloride, 188  
 iodometrically (*v*), 165  
 in bronze, determination of, and results, 287, 491  
 in presence of copper, 291  
 in tinstone, determination of, by bromate process, 264  
 by dry assay, 346  
 in white metals, determination of, and results, 291, 491  
 reduction of, 165  
 separation from certain elements, 317  
 from copper and lead, 291  
 from tungsten, 264
- Titaniferous iron ores**, analysis of, 302
- Titanium**, determination of (*v*), 189  
 colorimetrically, 244  
 in aluminium, 296  
 in iron and steel, 316  
 in ores, 293  
 in presence of iron, 293, 296  
 precipitation of, with cupferron, 303  
 separation from cobalt, nickel, manganese and zinc, 300  
 iron, 293  
 from other metals, 293  
 separations in iron and steel analysis, 316
- Titanous chloride**, preparation and use of standard solution, 185-190, 244
- Titration curves**, 208, 213  
 errors, 125  
 formol-, 132  
 micro-, 114
- Titre test for fats and oils**, 404
- Total hardness of water**, determination of, 363, 366  
 solids in milk, determination of, 375  
 in water, determination of, 350, 372
- Triangles**, 48
- Tropaeolin-D**, 119
- Tungsten in steel**, determination of, 314  
 separation from iron, 314  
 from silica, 314  
 separations in iron and steel analysis, 317
- Turbidimetric methods**, 249
- Turmeric-paper**, 121
- Twaddell degrees**, conversion to specific gravity, 513
- Type-metal**, analysis of, 290
- Ultra-Violet light**, fluorescence analysis in, 253
- Volts**, 106, 514-516
- Universal indicator**, 495
- Unsaponifiable matter**, in fats and oils, determination of, and results, 410, 508-513  
 in wax, determination of, 411
- Uranium**, determination of, by electrometric method, 219  
 reduction of, by zinc and sulphuric acid, 219  
 separation from certain metals, 317
- Uranyl acetate**, as indicator, 200  
 acetate or nitrate, standard solution of, for determination of phosphates, 203
- Urea**, determination of, by nitrometer, 480  
 in urine, determination of, 481
- Useful memoranda**, 518
- U-tubes**, filling of, 87
- Vacuo**, drying in, 30
- Vanadium**, in ferro-vanadium, determination of, 218  
 in iron and steel, determination of, 218, 315, 490  
 in presence of chromium, determination of, 218  
 in steel, determination of, by electrometric method, 218  
 oxidation and reduction of, 218  
 separation from certain metals, 317
- Vapour**, aqueous, pressure of, correction for, 462  
 table of pressures, 499  
 density, determination of, 446, 450, 454
- Vessels**, calibration of, 109-115, 461, 497
- Victor Meyer's method** for determination of vapour density, 454
- Vinegar**, determination of total acid in, 138
- Volatile matter in coal**, determination of, 318  
 organic compounds, combustion of, 434
- Volume of gases**, correction of, 461  
 units of, 106, 514
- Volumetric analysis**, typical processes, 104, 191  
 apparatus, table for use in calibration of, 497  
 standard solutions, correlation of, 128
- Wash-bottle**, 39  
 as aspirator, 86
- Washing precipitates**, process of, 37-40
- Washing-soda**, determination of water of crystallisation of, 137
- Water**, action of, on lead, 367  
 analysis of, 318-374  
 biological oxygen demand, determination of, 371  
 copper in, determination of, 367  
 density of, table, 196

**Water**, determination of, by difference (g), 91  
 by direct weighing (g), 92, 94  
 in substances which contain volatile matter, 406  
 in sulphates, 93  
 dissolved gases in, determination of, 136, 479  
 oxygen in, determination of, 369  
 expansion of, table, 196  
 free from ammonia, preparation of, 351  
 hardness of, determination of, 361-366  
 lead in, determination of, 243, 367, 374  
 mineral constituents in, determination of, 366, 368  
 oxygen saturation, determination of, 371  
 $P_{\text{H}}$  value of, 237  
 sample, collection of, 348  
 specific volume, table of, 196  
 vapour, pressure of, correction for, 162  
 table of pressures, 195  
 weighing in, 12

**Water-bath**, 35

oxygen saturation, determination of, 371  
 $P_{\text{H}}$  value of, 237

**Water-equivalent of a calorimeter**, 323

**Water-jacket**, 54

**Water-oven**, 26

**Water-pump**, 12

**Waxes**, acid value of, determination of, and results, 408, 508-513  
 constitution and properties of, 402  
 examination of, and results, 401-420, 508-513  
 mineral, examination of, 421  
 unsaponifiable matter in, determination of, 410

**Weak acids and bases**, determination of conductometrically, 224

**Weighing**, by direct method, 8  
 by method of swings, 7, 9  
 by substitution, 9  
 directions for, 9, 57  
 in water, 12  
 precautions during, 9  
 vessels for, 10

**Weight**, absolute, determination of, 9  
 burette, 114  
 of ml. of air, 516  
 of ml. of hydrogen, 516  
 of ml. and c.c. of mercury, 516  
 of ml. of nitrogen, 516  
 of water at different temperatures, tables, 196

**Weight**, primary unit of, 514  
 relation between volume and weight, 106

**Weights**, atomic, table of, front cover.  
 description of, 5  
 entry of, 10  
 testing of, 7

**Weights and measures**, tables of, 514, 515

**Werner-Schmidt's method** for determination of milk fat, 375

**White metals**, analysis of, and results, 290, 491

**Wijs' iodine solution**, preparation of, 412

**Wine**, determination of alcohol in, 520

**Winkler burette**, description of, 169  
 method for the determination of dissolved oxygen, 369

**Wolff's method** for determination of resin in soap, 421

**Working**, rules for, 57

**Xylene cyanol FF**, 162

**Zinc**, amalgam, preparation of, 448  
 determination of as oxide (g), 72  
 by electrolysis, 232  
 by electrometric method, 250  
 by nephelometry, 250, 368  
 by potassium ferrocyanide (g), 199, 224  
 and diphenyl-  
 benzidine (g), 200  
 by pyridine thioamide  
 reagent, 281  
 by conductometric method, 224  
 in aluminum alloys,  
 determination of, 298  
 in blends, determination of, and results, 261, 280, 492  
 in brass, determination of, and results, 286, 491  
 in German silver, determination of, 289  
 in water, 368, 474  
 separation from aluminum, iron and titanium, 390  
 from cadmium, copper, 261, 286  
 lead, 261, 286  
 from iron and manganese, 261  
 from nickel, manganese and cobalt, 283  
 in iron and steel analysis, 416  
 use of, as reducing agent, 447  
 evaluation of ores, 231, 289

**Zinc-blende**, analysis of, and results, 280-282, 492  
 determination of sulphur in, 493

## ANTI-LOGARITHMS

											Proportional parts									
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2	
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2	
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2	
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2	
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2	
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2	
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2	
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2	
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3	
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3	
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3	
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3	
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3	
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3	
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3	
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3	
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3	
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3	
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3	
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3	
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3	
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	2	2	3	3	3	
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	2	2	3	3	3	
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	2	2	3	3	4	
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	2	2	3	3	4	
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	2	2	3	3	4	
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	2	2	3	3	4	
27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	2	2	3	3	4	
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	2	2	3	3	4	
29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	2	2	3	3	4	
30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	2	2	3	3	4	
31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	2	2	3	3	4	
32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	2	2	3	3	4	
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	2	2	3	3	4	
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5	
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5	
36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5	
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5	
38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5	
39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	4	5	
40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	3	4	4	5	
41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	3	4	4	5	
42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	3	4	4	5	
43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	2	3	3	4	4	5	
44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	2	3	3	4	4	5	
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	2	3	3	4	4	5	
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	2	3	3	4	4	5	
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	2	3	3	4	4	5	
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	2	3	3	4	4	5	
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	2	3	3	4	4	5	
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	

## ANTI-LOGARITHMS

											Proportional parts.									
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	
50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7	
51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7	
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7	
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7	
54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7	
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7	
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8	
57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8	
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8	
59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8	
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8	
61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9	
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9	
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9	
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9	
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9	
66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10	
67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10	
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10	
69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10	
70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11	
71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11	
72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11	
73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11	
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12	
75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12	
76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12	
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12	
78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13	
79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13	
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13	
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14	
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14	
83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14	
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15	
85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15	
86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15	
87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16	
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16	
89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16	
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17	
91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17	
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17	
93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18	
94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18	
95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19	
96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19	
97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20	
98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20	
99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20	
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	



